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## XV Meeting of the Petrology Group of the Mineralogical Society of Poland

Powder Diffraction Rietveld Refinement Methods Workshop, 10-11<sup>t</sup>September, 2008

Abstracts





## SZKLARSKA PORĘBA, 9-14 SEPTEMBER, 2008

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## XV Meeting of the Petrology Group of the Mineralogical Society of Poland

Powder Diffraction Rietveld Refinement Methods Workshop

### organized by Mineralogical Society of Poland

together with: Committee on Mineralogical Sciences, Polish Academy of Sciences

Institute of Geological Sciences, Jagiellonian University, Krakow

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



# The Variscides in the West Sudetes: geological setting and review of tectonic models

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**Abstract:** The geological setting of the Sudetes in the NE part of the Bohemian Massif, the target area of the CEMC 2008, is outlined and the location of the fieldtrip sites on a geological sketch map is shown. References on selected petrological issues, palaeotectonic evolution and regional tectonic interpretations are also given.

Keywords: the Sudetes, Bohemian Massif, Variscan orogen, CEMC 2008

#### Introduction

The Sudetes in the NE part of the Bohemian Massif are comprised between two major NW-SE-trending fault systems, parallel to the SW margin of the East-European Craton (Fig. 1): the Odra Fault Zone in the NE and the Elbe Fault Zone in the SW (Fig. 2 inset). Parallel to them is the third important tectonic line, the Intra-Sudetic Fault Zone, cutting the area into two roughly equal parts (Figs. 1 & 2). In addition, the Sudetes area is divided by the oblique Sudetic Boundary Fault into two morphological domains: the mountainous SW part (the Sudetes Mountains) and the dominantly flat NE part, the Fore-Sudetic Block, largely covered by Cenozoic deposits (Fig. 2).



Fig. 1. Tectonic setting of the Sudetes in the Variscan Belt (from Mazur et al. 2006).

The entire Sudetes area is a complex structural mosaic composed of various types of geological units (Fig. 2), including: (a) basement units (fragments of Cadomian crustal blocks, variously metamorphosed Palaeozoic sedimentary successions and metaigneous complexes, all sealed with widespread Variscan granitoids), and (b) late- to post-orogenic (post-Variscan) cover, broadly ranging from the Lower Carboniferous up to Cenozoic deposits.



Fig. 2. Geological sketch map of the Sudetes (modified from Aleksandrowski et al. 1997). BB - Bardo Basin; ISF - Intra-Sudetic Fault Zone; KCU - Kamieniec Unit, KMC - Kłodzko Metamorphic Complex; KZG - Kłodzko-Złoty Stok Granitoid Massif; LG - Lusatian Granitoid Massif; NZ - Niemcza Shear Zone; SBF - Sudetic Boundary Fault; SSG -Strzegom-Sobótka Granite Massif; SZ - Skrzynka Shear Zone; ŚB - Świebodzice Basin. *Inset*: hachure - pre-Permian crystalline rocks; EFZ - Elbe Fault Zone; ISF - Intra-Sudetic Fault Zone; MGH - Mid-German Crystalline High; MO - Moldanubian domain; MS -Moravo-Silesian domain; NP - Northern Phyllite Zone; OFZ - Odra Fault Zone; RH -Rhenohercynian domain; SX - Saxothuringian domain. Age assignments: Pt<sub>3</sub> - Late Proterozoic; Cm - Cambrian; Or - Ordovician; D - Devonian; C - Carboniferous; Pz<sub>1</sub> - Early Palaeozoic. Location of the fieldtrip sites is indicated as A1 ... B3.

The major Variscan orogenic processes, including deformation, metamorphism, exhumation and intense granitic plutonism, echoed by syn- to post-orogenic volcanic

activity and sedimentation at the surface level, culminated through Late-Devonian to Permian times, ca. 380–280 Ma.

#### Geological ideas: past and present

Systematic geological investigations in the Sudetes started already in the 19<sup>th</sup> century (for review of early studies see Kryza et al. 2004). The Sudetes were variously interpreted either as a separate tectonostratigraphic unit within the Variscan Belt, referred to as Lugicum (Suess 1926), or their parts were correlated with the classical zones of the Variscides (Kossmat 1927): Moldanubian, Saxothuringian, and Rhenohercynian zones, more clearly defined to the west (e.g. Franke & Żelaźniewicz 2000, 2002).

Since the late 1980s, several models were proposed for the geological evolution of the NE part of the Bohemian Massif (Mazur et al. 2006, and refs. therein). Important constraints on these models are provided by tectonostratigraphic histories and structural data from various units, but strong arguments come also from recent petrological observations, such as the presence and position of ophiolites and MORB-type igneous rocks, HP-HT granulites, HP/T eclogites and blueschists, as well as from new geochronological data on magmatic, depositional and metamorphic events (Kryza et al. 2004, and refs. therein).

#### **Tectonic sutures: petrological constraints**

In the Variscan Belt of Central Europe, the following major tectonostratigraphic units (zones) and separating tectonic sutures can be defined (e.g. Franke & Żelaźniewicz 2000 and refs. therein), from north to south: Rhenohercynian Zone – *Rheic Suture* – Saxothuringian Zone (+ Mid-German Crystalline Rise) – *Saxothuringian Suture* – Moldanubian Zone (including Tepla-Barrandian and Moldanubian *sensu stricte* zones). Additionally, along the eastern edge of the Bohemian Massif, we find the NNE-SSE-trending tectonic boundary (Moldanubian Thrust and its northern prolongation), separating the core of the Bohemian Massif from the Moravo-Silesian Zone to the east. The Sudetes area appears to be a kind of structural "knot", where several major tectonic sutures meet. We can try to trace them using a range of structural and petrological criteria.

#### 1. MORB-type igneous rocks and ophiolites

These types of rocks, combined with other geological evidence, are commonly interpreted as traces of oceanic crust domains. Kryza (2007), partly based of earlier studies (Majerowicz 1981, Narębski 1992), distinguished two age groups of MORB-type igneous complexes in the NE part of the Bohemian Massif: (a) ca. 500 Ma mafic and ultramafic complexes being evidence of older, Cambro-Ordovician oceanic-crust domains (e.g. the Leszczyniec Complex in the eastern part of the Karkonosze-Izera Massif), and (b) ca. 400 Ma volcanic rocks and ophiolitic complexes indicating younger, Silurian-Devonian oceanic domains (e.g. the upper part of the Kaczawa Complex, and the Central-Sudetic ophiolites). The model in Fig. 3 shows: (a) contemporaneous intracontinental rifting and mature oceanic domains at ca. 500 Ma, as well as (b) younger, ca. 400 Ma oceanic domains.



Fig. 3. Palaeotectonic reconstruction of the evolution of the central-European section of the Variscides at 500 and 400 Ma (after Kryza 2007).

#### 2. Granulites and eclogites

HP-HT granulites are found in two different areas. In the Góry Sowie Massif (GSM), predominantly felsic granulites (peak conditions around 16-20 kbar, 900-1000°C; Kryza et al. 1996), are associated with mantle-derived mafic and ultramafic rocks (Brückner et al. 1991), all enclosed within HT-MP gneisses and migmatites. In the Orlica-Śnieżnik Massif (OSM), the felsic granulites, with subordinate mafic ones, occur within migmatitic gneisses. The age of the HP event has been estimated at ca. 390-400 Ma in both areas; however, the subsequent HT-MP event was dated, contrastingly, at ca. 370-380 Ma in the GSM, and ca. 340 Ma in the OSM (Kryza & Fanning 2007, Anczkiewicz et al. 2007, and refs. therein). This indicates different P-T-t and exhumation paths from the lower crustal levels, suggesting that the two granulite-bearing units belong to different terranes.

The OSM is also well known as a classical locality of eclogites (Smulikowski 1967). Their P-T-t paths were different from those of the granulites, and several tectonic and exhumation models have been proposed (Štipská et al.2004, Anczkiewicz et al. 2007, and refs. therein).

#### 3. Blueschists and mélanges

Important arguments for palaeotectonic reconstructions come from the presence, distribution and tectonic position of blueschist-facies rocks. They are found in the S and SE part of the Karkonosze-Izera Massif, where they were interpreted to delineate a possible tectonic suture formed after the closure of an oceanic domain separating possibly two

continental blocks (terranes?), Saxothuringian to the NW and Tepla-Barrandian (?) to the SE (Aleksandrowski & Mazur 2002, Oberc-Dziedzic et al., in press). In the Kaczawa Complex, the blueschist facies rocks are spatially associated with large bodies of sedimentary/tectonic melanges, providing arguments that the complex comprises fragments of a Variscan accretionary prism (e.g. Baranowski et al. 1990, Collins et al. 2000, Kryza 2008).



Fig. 4. Terranes in the Sudetes (after Aleksandrowski & Mazur 2002). Note that the Central Sudetic ophiolites have not been shown in that model.

#### Large-scale tectonic models

The growing amount of structural, petrological and geochronological data has revealed important contrasts in the provenance and evolution of various units of the Sudetes, and provided a basis for the application of the terrane concept, resulting in a range of controversial interpretations (e.g. Cymerman et al. 1997).

According to Franke and Żelaźniewicz (2000), the entire West Sudetes area, except for the Góry Sowie Massif interpreted as a part of Bohemia (or Tepla-Barrandian of the *sensu lato* Moldanubian Zone), belongs to Saxothuringia. Following Aleksandrowski and Mazur (2002), the Sudetic segment of the Variscan Belt was formed due to the accretion of five major and two or three minor terranes (Fig. 4). From west to east, the major terranes are: (1) Lusatia-Izera Terrane exposing Armorican continental basement reworked by Ordovician plutonism and Late Devonian – Carboniferous collision, showing Saxothuringian affinities; (2) composite Góry Sowie–Kłodzko Terrane characterized by polycyclic evolution (Silurian subduction, Mid- to Late Devonian collision, exhumation and extension, Carboniferous deformational overprint), with analogues in the NE Massif Central and Armorica; (3) Tepla–Barrandian Terrane distinguished to incorporate in its Sudetic segment the Nove Mesto Unit and the SW part of the basement of the Intra–Sudetic

Basin; (4) Moldanubian (Gföhl) Terrane comprising the Orlica–Śnieżnik and Kamieniec massifs, affected by Early Carboniferous high-grade metamorphism and exhumation; (5) Brunovistulian Terrane in the East Sudetes, set up on Avalonian crust and affected by Devonian to Late Carboniferous sedimentation, magmatism and tectonism. In that model, the major terranes are separated by two smaller ones squeezed along their boundaries: (6) Moravian Terrane, between Moldanubian and Brunovistulian, deformed during Early Carboniferous collision, and (7) South–East Karkonosze Terrane of the Saxothuringian oceanic realm affinities, sandwiched between the Lusatia–Izera and Góry Sowie–Kłodzko (together with Tepla-Barrandian) terranes, subjected to HP/T metamorphism and tectonised due to Late Devonian – Early Carboniferous convergence. The Kaczawa Terrane (8) in the NW, of oceanic accretionary prism features (Baranowski et al. 1990, Collins et al. 2000), metamorphosed and deformed during the latest Devonian – early Carboniferous times, may either be a distinct unit unrelated to the closure of the Saxothuringian Ocean or represent a continuation of the South–East Karkonosze Terrane (Mazur et al. 2006).

#### 2008 CEMC fieldtrips

The CEMC 2008 fieldtrips are proposed in the West Sudetes, and in the western and central parts of the Fore-Sudetic Block (Fig. 2). Pre-conference fieldtrip A2 presents selected structural problems of the Izera–Karkonosze Massif, defining tectonostratigraphic units based on petrological constraints, and interpreting their boundaries, as well as the major Intra-Sudetic Fault Zone. Two other excursions, A1 and A3, cover selected issues of mineralogy and petrology of complex Variscan granitic cycles in the NE part of the Bohemian Massif.

Post-conference fieldtrip B1 shows the HP-HT granulites, the enclosing anatexites in the Góry Sowie Massif, and their implications for exhumation models; the second part of that trip demonstrates the Central-Sudetic ophiolites (the Ślęża ophiolite) and their palaeotectonic significance. Fieldtrip B2 explores mineralogical and petrological features of the contact aureole of the Variscan Karkonosze pluton. Most of the fieldtrips indicate also various aspects of mineralogy, ore deposits and mostly abandoned mining activities, as well as geotourist potential of that area.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



#### Accessory minerals and Variscan plate tectonics

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The U-Pb isotope analysis of accessory minerals like zircon or monazite by ID-TIMS or SHRIMP techniques is the method of choice for precise and reliable dating of phases of magmatism and metamorphism within orogenic belts. Geochronological data derived from these tiny accessory minerals commonly serve as important basis for large scale plate tectonic interpretations (for the Central European Variscides see for instance Oliver et al. 1993; Friedl et al. 2000; Schulmann et al. 2005, 2008).

Recent research has shown that the growth and recrystallisation behaviour of zircon and monazite can be very complex (e.g. Geisler et al. 2007; Hansen and Harlov 2007; Harlov et al. 2007). This holds true, in particular, for high-grade metamorphic rocks, which record a history of subduction and subsequent isothermal exhumation. For example, monazite populations in Variscan high-pressure rocks from the Gföhl unit in the Bohemian Massif consist of at least three different age domains that assembled on the prograde path, at the PT peak, and during decompression (Finger and Krenn 2007). Monazite dating on such rocks is confronted with the perils to produce geologically meaningless mixing ages, as well as to misinterpret an obtained "real" age with reference to its geological context. The validity of macro-scale plate tectonic models therefore may directly hinge on the careful mineralogical study and correct genetic interpretation of microstructures in monazite.

Likewise, zircon ages for HP-HT granulites from the Variscan belt are not easy to interpret. There persists the fundamental question, whether zircon growth in these rocks occurs close to the PT peak (Kröner et al. 2000) or mainly on the decompression path (Roberts and Finger 1997). These uncertainties have greatly contributed to the unpleasant situation that in the Central European Variscan Fold Belt, the major subduction stages are still not unequivocally dated. Progress in the understanding of Variscan plate tectonics is thus intimately connected with our understanding of the growth and recrystallisation behaviour of the accessory zircons and monazites.

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#### General trends in HCNOS stable isotope geochemistry

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Stable isotope analysis of H, C, N, O and S is a powerful toll to trace the origin of substances, cycling of elements, reconstruction of chemical and physical conditions, dynamics and mass balance of minerals and rock-forming processes, and many others. Starting with late 40ties the role of stable isotope geochemistry in scientific research strongly increases. New applications and advances in technology resulted in continuous trends.

In this presentation the author will show some examples from various laboratories in the world and comment isotopic techniques applied with references to the most modern developments. Following terms can describe trends in isotopic techniques developments (listed but not organized due to any criteria): Smaller sample (micromoles to nanomoles); increased accuracy and precision, automatism: especially automatic preparation lines, automatic introduction of the gas analysed, automatic analysis, multicollector analysis (to analyse several isotopes simultaneously); increasing number of samples analysed, computer controlled preparation and analysis, stable isotopic analysis of other elements e.g. metals Cu, Fe, selective analysis of specific organic compounds, in situ analysis – laser ablation, ion microprobe, non MS stable isotopic analysis e.g. NMR, EPR, laser, negative ion MS analysis (e.g. Cl stable isotopes), on line preparation with GC, elemental analyser, etc., less home-made, practical monopoly of one company, increasing price of MS, increasing number of labs., new applications far from geosciences, decreasing use of vacuum devices and materials including liquid nitrogen, increasing use of ultra-pure gases (e.g. He, H<sub>2</sub>, CO, CO<sub>2</sub>, SO<sub>2</sub>, N<sub>2</sub>, and mixtures).

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## The fate of arsenic and antimony at polluted sites: an X-ray absorption view

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Arsenic and antimony are both toxic and undesired in the environment. We have investigated sites polluted by As and Sb (abandoned ore deposits: As and Sb, shooting ranges: Sb) and found distinct patterns in the migration of As and Sb. At the sites investigated, both As and Sb were efficiently scavenged by iron oxide minerals ferrihydrite, goethite, and lepidocrocite. These findings are supported by wet chemical, electron microprobe, X-ray diffraction, and Raman spectroscopy analyses.

Studies of Sb(V) adsorption on synthetic iron oxides were completely absent until now. We have investigated the geometry of surface complexes of Sb(V) on synthetic iron oxide minerals by extended X-ray absorption fine-structure (EXAFS) spectroscopy at the Sb *K* edge (30.5 keV). At lower surface loading, we could distinguish a bidentate-mononuclear complex with a Sb-Fe distance of 3.1 Å and a bidentate-binuclear complex with a Sb-Fe distance of 3.6 Å. As the surface loading grows, surface precipitation was detected from the observation of Sb-Sb neighbors in the EXAFS spectra.

Identical Sb bonding environment was found at two shooting ranges (Losone, Lucerne, Switzerland) polluted by Pb and Sb. Here, the steel mantles of the bullets weather to produce iron oxides which adsorb Sb. Organic matter may play a role in the retention of Sb, however, the bonding of Sb to organic material was difficult to prove because of the small scattering power of C/N/O.

Using EXAFS spectroscopy on the As *K* edge (11.8 keV), we have determined the local environment of As in As-rich hydrous ferric oxide (with up to 28 wt%  $As_2O_5$ ) from the abandoned Sb mine in Pezinok, Slovakia. The arsenate ions attach to the iron octahedra in a bidentate-binuclear (3.3 Å) and monodentate (3.6 Å) fashion. At very high As loading, we have also detected As-As pairs at a distance of 4.0 Å.

EXAFS spectra at the As K edge with a resolution of ~20  $\Box$ m on individual Fe,As-rich particles from Pezinok show spectra similar to the bulk ones, probably reflecting the presence of the same surface complexes. Currently, we are working on EXAFS data from Sb-rich grains (up to 65 wt% Sb<sub>2</sub>O<sub>5</sub>), where arsenic may be bound to antimony instead of iron. The goal of the study is to investigate the competitiveness of the two metalloids in phases depleted in iron and the results will be presented later.

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## Replenishment of felsic magma chambers by continuous inputs of mafic magmas: field evidence and fluid-mechanics experiments

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Widespread evidence indicates that magma chambers, sometime during their life span, are replenished by influxes of a more mafic magma and several processes subsequently acted to disperse the mafic magma in the felsic one, leading to different efficiencies of magma interaction. However, although the dynamics of magma interaction after the intrusion of the mafic magma are well understood, the mechanics of the initial stages of the interaction process, i.e. when the mafic magma enters the felsic magma chamber, remain essentially unknown and little studied. One possible reason for the paucity of works on these crucial stages of magma interaction is that they are rarely preserved in nature.

In this contribution we study different outcrops [i.e. Vegetatio Island, Terra Nova Intrusive Complex (Antarctica); Pleasant Bay layered intrusion, Maine (USA); Azetc Wash pluton, Nevada (USA)], in which the initial stages of invasion of mafic magmas into felsic magma chambers remained fossilized and extremely well preserved.

A wide range of contact morphologies, from rounded to interdigitate, between mafic and felsic magmas can be recognised in all three case studies. Morphology of the mafic/felsic interfaces is analysed by applying Fractal Geometry techniques with the aim to understand the origin of the varied morphologies by measuring the fractal dimension  $(D_{box})$ of the interfaces. Fractal dimension is a parameter that allows us to quantify the degree of irregularity of the interface between magmas and, in detail, the higher is the value of  $D_{box}$ , the higher is the irregularity of the interface. Results show that mafic-felsic contacts in all three outcrops are characterised by extremely variable values of  $D_{box}$  indicating, hence, a large variability in the irregularity of mafic-felsic contacts.

Morphologies of interfaces observed on natural outcrops are identical to those observed during "viscous fingering" processes induced by the displacement of a more viscous fluid by a less viscous fluid. In the viscous fingering phenomenon, the viscosity ratio  $V_R = \eta_I/\eta_2$ , defined as the ratio of the viscosity of displaced fluid ( $\eta_1$ ) to that of driving fluid ( $\eta_2$ ), influences the overall shape of fluid interfaces that range from regular when  $V_R \sim 1$  to extremely irregular for  $V_R >> 1$ .

Fluid mechanics experiments of viscous fingering have been performed by injecting water/glycerine solutions into pure glycerine at different  $V_R$  using the Hale-Shaw cell. Morphologies produced by the experiments are identical to those observed on natural outcrops supporting that the occurrence of viscous fingering processes between felsic and mafic magmas is a suitable hypothesis for explaining the varied mafic-felsic interface morphologies. As for natural structures the fractal dimension  $(D_{box})$  of simulated structures has been measured and a very good exponential empirical relationship between  $V_R$  and  $D_{box}$  derived. This empirical relationship is then used to estimate  $V_R$  of natural structures by

knowing  $D_{box}$ . Results indicate that for all three case studies magma interaction occurred between magmas with a wide range of  $V_R$ .

These results allow us to reconstruct the general evolution of magma interaction processes as characterised by continuous influx of the same mafic magma within a felsic magma chamber. At the beginning of the interaction process the viscosity contrast between magmas were large and this induced the development of very irregular morphologies of mafic-felsic interfaces. With the passing of time the resident felsic magma was progressively warmed up by the continuous influx of mafic magma and viscosity contrasts between magmas decreased favouring the development of progressively more regular morphologies. **Contributions** 

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## Heavy metal contamination at the Lubietová historic mining area (Slovakia)

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Hydrothermal Cu ( $\pm$  Fe, Co, Ag, Ni) mineralization in the surrounding of Ľubietová is situated in Ľubietová crystalline complex of Permian age. The complex consists of greywackes and arkose schists and conglomerates near of the contact with Lower Permian granitoid rocks. The ore mineralization is formed by chalcopyrite, Ag-tetrahedrite, hematite, arsenopyrite and pyrite. The main gangue minerals are quartz and carbonates (dolomite, siderite and ankerite).

The technogenous sediments, drainage water as well as the plants at the dump-field Podlipa at the Lubietová Cu-deposit are contaminated by heavy metals. During ca 200 years a limited group of plants (which is able to exist under such a fytotoxic conditions) was selected. The distribution of the heavy metals in sediments is very uneducable.

The surface water in the creek draining the valley along the dump-field is gradually contaminated by heavy metals leached from the technogenous sediments of the mining dumps. The drainage water contains high Cu (up to 2060 ppm), Fe (up to 584 ppm), Zn (up to 35 ppm) and sometimes also Co (up to 10 ppm) and Pb (up to 5 ppm) concentrations. The highest As concentration is 0.6 ppm. The As content is not high (reaching 0.061 ppm), both in the surface (and drainage) as well as in the groundwater. The speciation of the As shows only the presence of the less toxic As<sup>5+</sup>. The more toxic inorganic As<sup>3+</sup> is not present. The evidence for slow cementation process were found.

The presence of *Acidithiobacteria* or of sulphate reducing bacteria was not confirmed. The acidity both of the surface and groundwater is close to neutral pH (6.4 - 7.6) so the formation of acid mine drainage water is not probable.

At the old mine waste dumps there can be observed a natural installation of some plant species (*Pinus sylvestris, Betula pendula, Quercus petrea, Salix fragilis, Mentha longifolia, Acetosella vulgaris, Juncus articulatus*). Their development is specific to the local conditions: the low content of the essential nutrients and the high level of heavy metal content. The heavy metal content and the landscape features of the dump material are not favourable to the development of the vegetation. The individual parts of the plant tissues (roots, twigs/stems, leafs/needles or flowers/fruits) are differently contaminated by heavy metals and also the tissues are differently damaged. Comparison of individual types of plant tissues shows that the highest concentrations are in roots, than in leafs and stems and the lowest concentrations are in flowers, seeds and fruits. The plant tissues from the dump-field are heavily damaged and the growth of the current year shoots is extraordinary tight. The anomalous coarsening of the cell-walls, calluses and presence of resin-channels, as well as occurrence of hyfs in vessels indicate the plant defence reactions under the influence of
stress factors at the dump sites (absence of soil and water, the heavy metal contamination, mobility of the cohesion less slope material).

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### Gadolinite-group minerals: crystal chemistry, site occupancy and substitutions

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We studied crystal chemistry of the REE- and Be-bearing minerals – gadolinite, hingganite and minasgeraisite. The general formula could be written as  $W_2XBe_2Si_2(O, OH)_{10}$ , where Be and Si represent central cations of four tetrahedral sites. [9]-coordinated *W*-sites are occupied mainly by Y and REE, and by Ca in minority. *X*-site is octahedral and dominated by Fe (in gadolinite) but it could be vacant, balanced by  $2H^+$  (in hingganite). Gadolinite-group minerals are typical for granites and granitic pegmatites, but also for REE-rich metamorphic environments.

More than 180 published and unpublished electron microanalyses of gadolinite group minerals were calculated on the basis of  $2 (S^{6+} + P^{5+} + As^{5+} + Si^{4+} + Al^{3+})$  cations. Analyses of minasgeraisite were recalculated and classified as Ca- and Bi-rich hingganite-(Y). We obtained the continuous trend between the end-members gadolinite and hingganite with a slight Ca enrichment in hingganite. It could be caused by an input of the datolite molecule  $(Ca_2 \square BSi_2O_8(OH)_2)$ , which is X-vacant as well as hingganite. There could be observed the trend between hingganite and datolite, but only in the hingganite field (less than Ca = 1 *apfu*). However, this presumption can not be proven because the data on boron content are missing.

Two tested multi-site substitutions could have a major influence on the site occupancy of the *W*- and *X*-site. An effect of the first one, homilite substitution - CaFe(Y, REE)<sub>-1</sub> $\square_{-1}$  – can be proven from electron microanalyses. Verification of the datolite substitution (Ca $\square$ B(Y, REE)<sub>-1</sub>Fe<sub>-1</sub>Be<sub>-1</sub>) is limited by the undetermined B and Be contents. Other cations (e.g. Mg, Bi) have minor or local influence.

The enrichment of HREE (mainly those with ionic radii smaller than yttrium) in hingganite is remarkable. Lattice parameters of hingganite are decreased in comparison with gadolinite due to the presence of the vacancy in the octahedral X-site. A structural contraction could be the reason for selective input of REE cations with smaller ionic radii into the X-site.

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## Monazite as a tracer of metamorphic events in migmatitic granulites of South-Western Lithuania

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Monazites are important accessory phases in supracrustal migmatitic granulites from drillcores in south-western Lithuania (Lauksargiai-2, Lauksargiai-5 and Bliüdžiai-150 boreholes). They retain information not only on the age of the main thermal events in the host rocks but indicate the reactions and processes that release the components to build up/dissolve the new fractions of monazites (Williams et al. 2007).

Monazites from the Lauksargiai drillcores display several zones that differ in chemical composition and age. Several thermal events can be distinguished in a population of a few dozen monazite grains. In many crystals the high Y (up to 2.3 wt.%) cores record a 1.83-1.85 Ga event (some points are dated at more than 1.9 Ga that can be interpreted as an inherited age from the detrital stage). The younger 1.79-1.81 Ga event is characterised by low Y (below 0.15% wt.) which could indicate a period of simultaneous monazite and garnet growth. It documents the highest stage of metamorphism recorded by the biotitegarnet-plagioclase geothermobarometer at c. 800°C and 9 kbar. A population of low Y monazite (below 0.1 wt.%) records an age of 1.64-1.7 Ga which could indicate another thermal event. The age is attributed to a second stage of metamorphism at c. 700°C and 5-6 kbar. It is even possible to split this event with some uncertainty into two separate events (younger at 1.59-1.62 Ga and older at 1.71-1.72 Ga) according to the data from monazites analysed in the Bliüdžiai 150 drill core, where a 1.72 Ga event can be interpreted as a partial breakdown of garnet and crystallisation of cordierite due to the lower temperature and pressure of c. 780°C and 5-6 kbar. Such an interpretation could be supported by moderate high Y content (1.3-1.4 wt.%). The younger event is rather an indicator of additional melt creation, as indicated by lower pressures of 3 kbar.

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#### Olivine with perfect cleavage from Yoko-Dovyren Massif, Russia

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The olivine with perfect cleavage is very rare. To date, it has been described in just a few places worldwide (Siskiyou County-California, USA; Dabie Shan, China; Chalk Hills, Salem, Tamil Nadu, India; Oeyama, Japan). For the first time, the olivine showing perfect cleavage parallel to planes (010) and (100) is described herein. It occurs in the skarns formed in carbonate xenoliths and in the magmatic rocks in dunite-troctolite zones (Proterozoic Yoko-Dovyren Massif, Northern Baikal Region, Russia). Mg-skarns bodies are formed from the silica-poor dolomitic xenoliths by interaction with mafic magma from Yoko-Dovyren intrusion. The mineral association for the olivine zones of the skarn includes forsterite  $(Mg_{1.78}Fe_{0.18}Ca_{0.02}Cr_{0.02})SiO_2$ , Zr bearing perovskite, spinel  $(Mg_{0.79}Fe^{2+}_{0.21})(Al_{1.80}Fe^{3+}_{0.17}Fe^{2+}_{0.01}Ti_{0.01}Cr_{0.01})_{\Sigma 2}O_4$ , and subordinate monticellite  $(Ca_{0.98}Mg_{0.02})(Mg_{0.81}Fe_{0.19})(SiO_4)$ . Monticellite forms xenomorphic grains (100 µm) and oriented plate inclusions in olivine (>10  $\mu$ m). Exolutions of monticellite are parallel to (010) and (100) of olivine. The high temperature of-crystallization is indicated by the high Ca content in the olivine. The exolutions of monticellite were formed upon cooling and the perfect cleavage is activated by subsequent heating. The proposed explanation doesn't rule out an alternative model: formation of olivine crystals at high temperatures after humite group mineral, associated with preservation of planar (humite) defects in olivine.

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# Si-deficient vesuvianite from jade-like rodingite from Eastern Sayan, Russia

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A Si-deficient vesuvianite has been found as rock-forming mineral in violet jade-like rodingites from the Ilchir River overhead in the Ospin-Kitoy ophiolitic massif, Eastern Sayan. The rodingites are Ca-rich and Si-undersaturated metasomatic rocks. They formed during serpentinization of ultramafic rocks and are genetically associated with Cametasomatism of varied types of silicates rocks. The violet jade-like rodingites are fine grained rocks with massif structure forming lenticular bodies up to few meters in size. They are mainly composed of vesuvianite, with subordinate hydrogarnet, clinochlore, zircon and baddeleyite. The rock is separated from lisardite serpentinites by a thin chlorite zone. Mnbearing minerals of pyrophanite-ilmenite series found in the chlorite zone can be interpreted as indicators of oceanic floor metasomatism. EMPA data indicate that vesuvianite contains 16.9-17.63 Si pfu: Ca<sub>19</sub>(Al<sub>11.8</sub>Mg<sub>1</sub>Fe<sub>0.3</sub>)<sub>\Sim13.1</sub>Si<sub>17.2</sub>O<sub>67.1</sub>(OH)<sub>10.9</sub>. The low content of Si is connected with a hydrogarnet-type substitution in vesuvianite structure, where isolated tetrahedra  $(SiO_4)^4$  is replaced by  $(H_4O_4)^4$  tetrahedral. A series of Sideficient vesuvianite can be expressed by the formula  $X_{19}Y_{13}T_{0.5}(Si_2O_7)_4(SiO_4)_{10-1}$  $_{x}(OH)_{4x}W_{10}$ , where x is <3. Mineral association, structure and chemical data of violet jadelike rodingites from Eastern Sayan indicate that they are early generation of rodingites, which were developed during oceanic floor metasomatism stage.

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### Micromorphology of quartz grain surfaces from mineral-organic soils and sediments from the Unislaw Basin (Poland)

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Quartz grains are common in the sandy fraction of sedimentary rocks and soils. Surface parameters of this mineral preserve record of the sedimentary environment, type of transportation, deposition, and soil processes. That is why the micromorphological analysis of quartz grains by scanning electron microscopy (SEM) can be useful in reconstruction of their genesis, site of creation as well as post-sedimentation and soil processes occurring after the deposition. The 1-0.1mm quartz grain fraction separated from two profiles of alluvial soils derived from organic-mineral sediments (gyttia) of the lake-rich origin, located on a biogenic plain of the Unislaw Basin, were subject of SEM micromorphological analysis. The analysis shown that despite differences in the sedimentation environment of the sediments under study quartz grains from sandy fraction are very similar. It suggests a common origin as well as lack of the impact of the post-sedimentation processes. Despite rounding the majority of grains shows decollments, fissuring and splits on their surface, probably developed during glacial period. V-shape scratches originated during later water transport which washed-out clay and deposited quartz in the analyzed sediments. A majority of the grains did not show symptoms of chemical weathering. The only exception was sediment of the argillaceous-calciferous gyttia from the profile 2. In the last case amorphous silicate was detected on the surface of the grains. However, this was probably related to the earlier chemical weathering, because conditions occurring in the sediments under study (a high concentration of  $CaCO_3$  and a high pH) could not support weathering of this kind. No other symptoms that could indicate the existence of such weathering conditions over the post-sedimentation period and during the creation of the analyzed soils were detected.

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## Morphological changes on the quartz crystals during leaching at higher temperatures and pressures in aqueous fluids

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Morphological changes on the quartz crystal were studied after an experiment in a thermo reactor type Parr 4652. A volume of the reactor is 500ml and this apparatus simulates temperature up to 500°C and pressure up to 340 bars. This ability was used for a study of the hydrothermal leaching of the quartz at higher temperatures and pressures in aqueous fluids.

Morphological changes in the structure of quartz were apparent as a result of an experiment with the use of a thin plate cut from crystal of quartz with noticeable two zones (cut was perpendicular to c axis). This thin plate with an initial weight of 0,7555g was exposed to following conditions: 65 ml of distilled water, temperature of 365°C and pressure of 185 bars. The experiment was carried on for 7 days. These conditions led to loss of 9.48 % from the initial weight (the final weight was 0,6839g). Microprobe analysis of the quartz before the experiment showed that the crystal was almost pure except for few inclusions of chlorites.

An observation using the *scanning electron microscopy* showed different morphological structures caused by the leaching in each separate crystal zone within one crystal. In outer zone the leaching lead into disordered fissures or openings without the remarkable crystallographic symmetry. They are visually similar to karst grikes. Signs of the leaching in the inner zone were more varied. It was possible to observe either trigonal and pseudohexagonal etch pits (approximately  $25-100\mu$ m in diameter) or newly formed small quartz crystals (approximately  $10-80\mu$ m in size). The possible explanation of the formation of the quartz crystals is too slow cooling of the reactor after the experiment. This could cause new crystallization of the outspread quartz from the liquid.

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# Magmatic sulfur mineralization within transitional dunites of the Bulqiza Ultrabasic Massif (Albania)

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The ultramafic massif of Bulqiza belongs to the eastern belt of the Jurassic ophiolites in Albania. Its geological section, from the bottom to the top, consists of three rock sequences: (i) tectonic sequence (harzburgite and dunite); (ii) transitional zone (massive dunite) and (iii) magmatic sequence (wehrlite, pyroxenite and gabbro). The Bulqiza massif is the most noted due to its chromium-bearing potential. The most economically important chromite ore bodies, which belong to the metallurgical type (rich in Cr), are found in the upper part of the tectonite sequence and in the transitional zone.

In addition of abundant chromite mineralization occurrences, a scarce sulfur mineralization is hosted by massive dunites of the transitional zone. The sulfur mineralization consist only of pentlandite which occurs either as inclusions within chromite or it fills the interstitial spaces between olivine and chromite. The pentlandite, that shows a relatively stable composition, consists of Fe (x=33,29 %), Ni (x=31,43 %) S (x=33,60 %), whereas Zn and Mn are scarce. The Ni/Fe ratio is always less than one. Secondary magnetite, awaruite and native copper have replaced the pentlandite in the periphery, along fissures or as small spots on the grain surface.

A magmatic origin of this mineralization was considered based on the value of the ratios Cu/(Cu+Ni)=0,14-0,19, Ni/Co=19-71 and Pt/(Pt+Pd)=0,21-0,58, stable composition of petlandite, lack of arsenides and, finally, isotopic composition of sulfur ( $d^{34}$ S=-0,6 - +0,3 %). The pentlandite probably crystallized from the same magmatic melt that gave interstitial clinopyroxene and plagioclase. Such a conclusion is favored by the following findings:

- The sulphides are found only within the impregnated dunites, whereas in the nonimpregnated dunites they are sparse or absent.
- The accessory chromite in impregnated dunites is rich in Al ( $Al_2O_3 = 25\%$ ), whereas in the non-impregnated dunites it is rich in Cr.
- The spherical form of the included chromite in pentlandite was probably caused by partial melting of its periphery by sulfur fluid.
- The interstitial structure of pentlandite with respect to olivine and chromite is similar to that of impregnated clinopyroxene and plagioclase.

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### Mineralism – an application of crystallographic-mineralogic-petrologic imagery in art

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This paper presents an attemt to show the evidence that the Crystallographic-Mineralogic-Petrographic imagery not only offers a scientific information, but it preserves in its inner a complex and interesting artistic value. On the other hand, the art technics represent the best way of communication of this scientific information to people.

The old people say: "Don't hit the stone as it hurts". This publication aims to prove that more than a metaphore, this is a reality.

The photography was always used as a technique to produce albums of minerals with beautiful crystals and special forms. But the world of minerals and rocks represents much more.

Through presentation of the microscopic and macroscopic images of minerals and stones by menas of different figurative techniques (pictures in oil, graphic, sculpture, instalations or poems), not only the outer view of a stone can be presented, but the inner side of it, its life, its soul as well.

An universal parallelism exists between the life of the rock and minerals on one side and human being life on the other side. The laws of life are the same: it begins with an embrion, it grows through struggle for existence, and, at the end, it dies by being transformed. This life has its colours and shades, has pains and tears, sounds and music. In my opinion, exept for a different status of the subject, nothing is different in these two different lives. One more solid, the other more liquid; one organic, the other inorganic. It is the virtue of the human being to know and understand this life. To do this, one must first love it.

This parallelism was called "Mineralism" and it represents a new effluent in art. In fact, it is an application in art of Crystallography-Mineralogy-Petrography sciences. It is twice art: art in presentation and art in communication.

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### Mineralogical study of zeolites from plagiogranitic rocks, Albania

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Plagiogranite - quartz diorite rocks represent the uppermost part of the plutonic section of the eastern Albanian ophiolites. They are widespread along the north- eastern sectors of the ophiolitic complex. Locally, intrusive contacts with gabbroic and volcanic rocks is observed.

The zeolitization represents one of the most developed secondary processes that have affected the plagiogranitic rocks. The zeolite has filled both the thin veins and small cavities of the rock. It is scarcely found inside the sulfur mineralization. Seven zeolite-bearing plagiogranites have been sampled. Analyses of the mineral phases have been carried out using electron microprobe, SEM and XRD. Whole-rock composition was determined by XFR (major and trace elements). The thermal behaviour was tested by TG and DTA.

The zeolite-bearing rocks are very soft because of the intensive alteration they underwent and their color is white-rose due to their mineralogical composition. Their mineralogical composition includes mainly (55-60%) plagioclase and quartz, followed by zeolite (30-35%) and, subordinate amphibole and chlorite (10%). The SiO2/Al2O3 ratios in the plagiogranites range from 2.6 to 5.9. The plagioclase composition ranges from andesine to albite. The zeolite belong to Laumontit - Leonhardit series. The crystals of laumontite fill the cavities and veins in plagiogranite. The secondary Ca-type zeolite contrast the primary Na-type feldspar of the rock. Thermal effects associated with the loss of water are observed at 99°C, 240.8°C, 400.62°C.

Both the geological setting of the zeolitic mineralization within the plagiogranites and their mineralogical composition indicate their formation by hydrothermal processes. The Ca-zeolitic mineralization was formed later due to the alteration and substitution of the Na-feldspar.

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### Mineral and chemical composition of aeolian dust from a fall in march 2007 in the Tatra Mountains (Southern Poland)

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Aeolian material deposited with snowfall during the night of 23/24 March 2007 was collected on 25th March 2007 at the Hala Gasienicowa meadow (at 1510 m ASL) in the Tatra Mountains (Southern Poland). Dust is composed mainly of quartz with a subordinate amount of feldspars (plagioclases and K-feldspar), micas, I/S minerals and traces of kaolinite. Its grain size varies from below 1  $\mu$ m to 25  $\mu$ m but bigger grains are also present (mica flakes up to >120  $\mu$ m in diameter). Aggregates composed of mica and quartz grains which also contain organic matter and iron oxides are common. The chemical composition (SiO<sub>2</sub> >65 wt.%; Al<sub>2</sub>O<sub>3</sub> ca. 17 wt.%; Fe<sub>2</sub>O<sub>3</sub> ca. 9 wt.%; K<sub>2</sub>O ca. 3.5 wt.%) correlates well with their mineral composition. A determination of the geographic localization of the source area of the dust based on its mineral and chemical composition is impossible.

Pollen of trees and shrubs (such as Alnus, Pinus, Betula, Corylus, Carpinus, Acer, Ulmus, Picea, Fagus, Salix) and herbs (Compositae, Cyperaceae, Chenopodiaceae, Caryophyllaceae) were determined in the dust. The composition of the pollen spectrum corresponds with the local vegetation of the Carpathian Mountains. Thus, it indicates a local (200-300 km) source area of the aeolian material.

Several dust falls were noted in Southern Poland in XIX and XX centuries. Several mineralogical analyses of the dust are available in literature (*cf.* Manecki et al. 1978). The source area was usually localized in the area between the Black Sea, the Sea of Azov and the Caspian Sea. Dust material deposited in 2007, which is derived from the local source area in the Carpathians, is very similar in its mineral composition and grain size to the material from other dustfalls noted in Southern Poland. The lack of calcite in the local material is the only significant difference.

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### A role of structural interaction between minerals in mineralogenesis (based on the example of graphite)

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In Precambrian complexes of the Ukrainian Shield the phenomena of steady natural intergrowth of graphite with other minerals which have, at least, the same symmetry but different chemical bonds are rather widely encountered. The following pairs look most contrasting: biotite (C2/m) - graphite (6/mmm), muscovite (C2/m) - graphite (6/mmm), molybdenite (6/mmm) - graphite (6/mmm), nepheline (6/mmm) - graphite (6/mmm), pyrrhotite (6/mmm) - graphite (6/mmm).

Especially, close associations between micas and graphite are frequently empirically established at mineralogical and at even larger scale. Close similarity between these minerals has led to the use of the term «Graphitglimmer» in general geological practice. The largest deposits of graphite in the Ukrainian Shield are located within mica gneisses and shists where graphite generally occurs as natural intergrowths with micas (biotite, muscovite, sericite).

Detailed X-ray investigation of lamellar monocrystals of graphite has shown, that they are usually represented by twins. These twins generally have intergrowth plane of (0001) and are characterized by rotation of individual crystals by 30° around (0001). More complex intergrows are also found. Some crystals show weak texturing with azimuthal angle of dispersion of  $\Delta \phi$  5...12°. Biotite which is found in intergrowths with graphite is related to IM d. Intergrowths are formed along (0001) plane. Thus, the biotite and graphite are found in natural orientation, when (001) plane of biotite is parallel to (0001) of graphite and b = [010] of biotites is parallel to a = [1010] of graphites.

It is widely known that structural relationship between associated minerals can be determined by epitaxy or other phenomenons that are closely related. The important factor that determines possibility of epitaxy is the change of free energy of boundary between intergrowing phases. If stability of epitaxial intergrowth depends on degree of adhesion of growing layers to mineral-substrate, the necessary condition of its growth is positive value of critical oversaturation. The importance of epitaxy for ore formation processes is manifested by the fact that intergrowth of structurally similar (symmetricaly similar) minerals can occur at much smaller deviations from equillibrium which are necessary for the start of crystallization. Thus, oriented crystallization of a mineral on another structurally similar mineral occurs at slightly different conditions of thermodynamic equillibrium.

A new mineral which is far from oversaturation with respect to the solution infiltrating steadily around the mineral grain playing a role of a substrate, can precipitate on this substrate. It is that intergrowths in which the lowest-energy interface of crystals is realized. The effect of mineral - substrate on crystallization of other phase might be one of the key factors in understanding the observed structural interaction between minerals.

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### Origin of a syenitic dike by a flowage differentiation (Modra Massif, Western Carpathians): evidences from the rock-forming and accessory mineral assemblage

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Dikes occurring in the area of the Dolinkovský vrch Hill (Malé Karpaty Mts.) are, according to the geochemical data, the derivates of the Middle Carboniferous Modra I-type granitoid massif. They intrude both metapelitic and carbonatic wall rocks. Dikes in the metapelites and metabasites (x meters in width) in the centres show syenogranitic to syenitic composition. The syenite dike is a coarse-grained rock, with an average grain size around 5 mm. Euhedral K-feldspar forms 73.7 vol. % and is partly altered by postmagmatic fluids (kaolinized). Boundaries between the K-feldspar grains are straight, without diffusion features. Strongly accumulated K-feldspars form a cumulate structure and give the rock a syenitic character. Earlier authors considered them to be the products of K-metasomatism, but now a process of K-feldspars show a bell shape distribution indicating the magmatic origin and pointing to the fractionation of K-feldspar from the melt. Syenitic rocks contain even higher Ba, mainly due to an accumulation of K-feldspar as a carrier of Ba (2900 – 3200 ppm).

The crystallizing K-feldspar generates a chemical boundary layer (BACON 1989), enriched in Ca, P and Si (relevant parameter in the apatite saturation process; HARRISON & WATSON 1984, PICHAVANT et al. 1992), which upon cooling stabilizes apatite. Apatite, abundant in syenitic rocks and enclosed mainly in interstitial quartz, is interpreted as a crystallizing phase in a Ca, Si and P-rich boundary layer, adjacent to K-feldspars. Needles of apatite are typically intergrown with the outer zones of K-feldspars and enclosed in a matrix of quartz  $\pm$  albite. It is proposed that various degrees of the subsequent K-feldspar compaction and quartz + albite melt expulsion are responsible for the correlation of K2O with P, and increased the P concentration up to 0.9 wt.%. In this way, almost all Ca in high P samples (syenite) is bound in apatite. The fractionation of amphibole present in some dikes may have increased the A/CNK ratio to the values exceeding 1.05, sufficient for a delay in apatite crystallization and enabling a growth of P in the system. During the following compaction, quartz - albite melt was expelled, leaving a cumulate to various degrees enriched in K-feldspar and apatite. The dikes cutting the limestones show a wide contact aureola of calc-silicate hornfelses, suggesting an extensive fluid interaction between the magma and the wall rock. The maximum pressure, estimated from Al-in-hornblende thermobarometer, is less than 150 MPa.

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# Bi sulphosalts from the antimony mineralization (Western Carpathians)

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Bi sulphosalts form a part of the tetrahedrite stage of the antimony mineralization in the Western Carpathians crystalline basement. This stage was identified at several localities in the Gemeric and in the Tatric tectonic Units. In the Tatric Unit (Klačianka, Dúbrava and Mlynná dolina – Hviezda localities) the tetrahedrite stage is younger than the main antimony stage, whereas in the Gemeric Unit (Betliar locality) it is older. The main ore mineral in all localities is tetrahedrite, accompanied by Fe-dolomite, quartz, sphalerite, chalcopyrite, bournonite and Bi-bearing sulphosalts in the Gemeric Unit, and by Fe-dolomite, quartz, barite, gold, pyrite, bournonite and Bi-bearing sulphosalts in the Tatric Unit.

The following Bi-bearing sulphosalts were identified: minerals of the kobellite-tintinaite series (KTS), members of the bismuthinite-aikinite series (BDS), minerals of the chalcostibite-emplectite series, Bi-bearing zinkenite, Bi-bearing jamesonite and Bi- bearing bournonite. The most common sulphosalts are members of the KTS. They form blebs, inclusions or needles in tetrahedrite. Members of BDS are less common and were identified in the Dúbrava, Klačianka and Hviezda. Other sulphosalts are rare. Bi-bearing zinkenite was identified at Dúbrava and Betliar, Bi-bearing bournonite at Dúbrava, Bi-bearing jamesonite at Hviezda and members of the chalcostibite-emplecite series at Klačianka and Dúbrava. The content of Bi in the minerals of the KTS is variable. It varies from the 12.5-19.5 wt. % at Dúbrava, through 20.4-22.6 wt. % at Hviezda, up to 24.8-27.8 wt. % at Betliar. The ratio Sb/(Sb+Bi) changes from 0.66-0.78 at Dúbrava, through 0.60-0.65 at Hviezda, up to 0.51-0.56 at Betliar. All studied samples fall into the tintinaite field, especially the Dúbrava ones. The BDS are represented mainly by Sb-rich bismuthinite, Sbrich krupkaite is rarer. The content of Sb in bismuthinite varies from 3.9-8.34 wt. % at Klačianka, through 9-26 wt. % at Hviezda, up to 26.8-27.4 wt. % at Dúbrava. The  $n_a$  – degree of aikinite substitution is very similar at Hviezda (1.5 - 4.8) and Dúbrava (1.6 - 2.5) but different and more variable at Klačianka (4.7 - 12). Sb-rich krupkaite with n<sub>a</sub> from 51 up to 53.24 contains from 26.5 up to 27.5 wt. % of antimony, which gives the Sb/(Sb+Bi) ratio close to 0.7. The content of Bi in the antimony sulphosalts is as follows: bournonite up to 1 wt. %; zinkenite from Betliar - 0.6 to 8.1 wt. %, and from Dúbrava - 8.2 to 8.7 wt. %; jamesonite from 25.3 up to 27.5 wt. %; chalcostibite from Dúbrava - up to 10.5 wt. % and from Klačianka - 8.6 to 33.42 wt. %. We suppose that Bi-rich sulphosalts were formed by metasomatic processes, where Bi-rich fluids overprinted the previous Sb sulphosalts.

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### Columbite-(FE)-tantalite-(FE) and tapiolite-(FE) in the leucogranites from the Považský Inovec Mts., Western Carpathians, Slovakia: chemical composition and evolution

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Accessory Nb-Ta oxide minerals were identified in the pegmatitic leucogranites near Duchonka, Považský Inovec Mts., Western Carpathians, Slovakia. The studied leucogranite is a medium to coarse-grained rock, which consists of quartz, K-feldspar, plagioclase (An<sub>04-</sub> 28), muscovite, sillimanite, almandine-spessartine, rarely Hf-rich zircon (6-22 wt.% HfO<sub>2</sub>), apatite-(CaF) and Nb-Ta minerals. The rocks can be geochemically characterized as highly fractionated leucogranites with S-type characteristics. They are comagmatic with other Lower Carboniferous granitic rocks of the Bojná Massif. Columbite-tantalite occurs as prismatic crystals, 30-350 µm in size, in association with quartz, alkali-feldspar and muscovite. The mineral shows oscillatory zoning with central parts enriched in Nb and rims enriched in Ta. Locally, there is a reverse trend of zoning (decrease of Ta towards border parts), or irregular convoluted zoning of border parts, as a result of the subsolidus replacement processes. The composition of columbite-(Fe)-tantalite-(Fe) shows a relatively constant Mn/(Mn+Fe)=0.20-0.27 (locally 0.35-0.40), and an extreme range of Nb-Ta fractionation: Ta/(Ta+Nb)=0.18-0.72. Group of analyses with Ta/(Ta+Nb)=0.63-0.72 are in the field of the miscibility gap between tantalite and tapiolite. Contents of Ti, W, Sn, Mg and other elements are low, locally slightly higher Zr and Pb contents occur (≤0.6 wt.%  $ZrO_2$  and  $\leq 1.2$  wt.% PbO). Rare tapiolite-(Fe) forms discrete crystals, ca. 15-75 µm in size. The tapiolite-(Fe) is homogeneous with Mn/(Mn+Fe)=0.03-0.04 and Ta/(Ta+Nb)=0.88-0.97; Ti and Sn contents are  $\leq 1$  wt.%.

The Nb-Ta association in the Považský Inovec leucogranites is unique within the Western Carpathians. It extends into the tantalite-tapiolite miscibility gap. The presence of tantalite-(Fe), with unusually high Ta content, could indicate its metastability or a smaller range of miscibility gap between tantalite and tapiolite in the leucogranites in comparison to the granitic pegmatites (cf. Černý et al., 1992).

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# Ellestadite-(F) – a mineral formed in the overburned coal dump (Upper Silesian Coal Basin)

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Ellestadite is a rare mineral found in nature in skarns or metamorphosed limestones. It is also known from the burned coal dumps, where its formation is possible in the presence of carbonaceous and carbonate rocks as a result of pyrometamorphism of sedimentary rocks.

Fluor-ellestadite is a member of the apatite-ellestadite solid solution group of the general formula  $Ca_{10}(SiO_4)_{3-x}(SO_4)_{3-x}(PO_4)_{2x}(OH, F, Cl)_2$ , where x varies from 3 in apatite to 0 in ellestadite. The presence of the CO<sub>3</sub> group is also possible. Each kind of ellestadite prefers different environment of its formation. Ellestadite containing fluor is frequently found within the overburned coal waste dumps, chlor-ellestadite can form mainly in supergene cave deposits whereas hydroxy-ellestadite in calc skarns.

A 6 mm in diameter nest of blue mineral was found in the remainder of the quenched dump of closed in December 1995 Saturn Coal Mine in Czeladź, near Katowice (Upper Silesian Coal Basin). This mineral was found in the part of the dump which was affected by the fire and is strongly overburned. Using scanning microscope, 10-60  $\mu$ m ellestadite crystals of different chemical composition were discovered together with calcite. Analytical points (EDS) revealed divergence in (SiO<sub>4</sub>), (SO<sub>4</sub>) and (PO<sub>4</sub>) content within different crystals of ellestadite. BSE images and microprobe analyses show rather homogeneous chemical composition within analyzed grains. On the basis of microprobe analyses the following formula was calculated: (Ca<sub>9.98</sub>Mn<sub>0.02</sub>)<sub>10</sub>(SiO<sub>4</sub>)<sub>2.75</sub>(SO<sub>4</sub>)<sub>2.13</sub>(PO<sub>4</sub>)<sub>0.04</sub>(F<sub>1.44</sub>Cl<sub>0.04</sub>)<sub>2</sub>. As the formula is not completed, the lack of 0.49 a.p.f.u. was explained as a possibility of existence of (CO<sub>3</sub>) or (OH) groups. Raman spectroscopy confirmed the presence of both CO<sub>3</sub> and OH groups.

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### Petrology and geochemistry of the neogene rhyolites from the Central Slovakia Volcanic Field, Western Carpathians

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The Central Slovakia volcanic field (CSVF) is a product of Neogene volcanic activity linked to the collision of the Western Carpathians with the stabilized European platform. The volcanic activity started in the Middle Miocene with the production of andesites. The rhyolite volcanism operated during the Upper Sarmatian with the production of pyroclastics, extrusive domes and lava flows. After the rhyolitic volcanism ceased, an activity proceeded with the eruption of subalkaline basalts and later alkaline basalts. Rhyolites have mainly porphyric textures, but aphyric types and obsidians are also present. Phenocrysts consist of alkali feldspars, plagioclase, biotite, quartz with scarce Fe-Ti oxide or amphibole and hyperstene. Accessory phases include zircone, allanite and rare apatite. The important petrographical feature is a separate presence of plagioclase, plagioclase with sanidine, or sanidine in phenocryst assemblages. Rhyolites are generally peraluminous with ASI > 1 and subalkaline based on TAS criteria. K<sub>2</sub>O/Na<sub>2</sub>O ratio corresponds with shoshonitic and ultrapotassic character. As for a peraluminous character, low TE and Ga/Al -(Zr, Nb) rhyolites belong to the transition S-A types. Petrology study, based on two feldspar thermometry, i.e. Pl-Amf thermometry and Amf barometry, yields magma temperatures between 700-800°C and pressures ~ 6 kbar. Estimated H<sub>2</sub>O content in the primary magmas was more than 4 wt.% and probably did not exceed 5 wt.%. Some rhyolite magmas degassed water during storage in the upper parts of crustal magma chambers to create stratified setting of immiscible magmas. Such conditions affect syneruption mingling, frequently documented by a field and a petrographical studies. Geochemistry of trace elements, especially a topological approach to Nb-La-Zr-Ti-Y systems, identified three distinct petrogenetic groups of rhyolites. Each of them is straight controlled by an individual magmatic process. Trace element chemistry of the first group is controlled by a simple melting process without any fractional crystallization signature. Such conditions could be explained by restricted crystal settling because of high magma viscosity and variable mixing between evolved liquid and crystal- rich magma. Composition of the second group results from a different style of melting with the apparent fractional crystallization effect. The third group shows perfect mixing between the group II and the differentiated melts observed as aplites of the Hodruša granodiorite complex. Rhyolites of CSVF are clearly distinct from the associated older andesites, younger andesites and alkali basalts. Peraluminous S/A rhyolites with different feldspar association and chemical composition formed as the result of dehydratation melting of diverse metasediments in the conditions exceeding 800°C and 6 kbar (20 km). This melting must have been triggered by the heat influence of uderplating basaltic magmas. This idea is supported by the space and time association of S-A rhyolites with basalts of different genesis, ubiquitous worldwide.

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# Post-magmatic hydrothermal vein mineralization in granitic rocks: T-X evolution, fluid inclusion study

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This contribution briefly summarizes the investigation of fluid inclusions in hydrothermal vein mineralization and fracture fillings of three granitic massifs of the Czech Republic: the Podlesí granite stock, which represents the most fractionated part of the late Variscan Nejdek-Eibenstock pluton in the western part of the Krušné hory Mts; the Jizera Granite, one of the dominant rock types of the Variscan Krkonoše-Jizera composite massif; and the Melechov granitic massif in the northern part of the Moldanubian Pluton. Several types of mineralization were distinguished based on the fluid inclusion parameters:

1) Biotite-rich and quartz-rich greisens – up to 500 °C

Two-phase vapour-rich aqueous inclusions were found in the greisens of the Podlesí granite stock, homogenization temperatures range from 370 to 420 °C, salinity of the aqueous solution is between 4.7 and 11 wt. % NaCl equiv. (Dobeš, 2005). Two types of coexisted fluid inclusions were observed in the greisens of other localities of the Krušné hory Mts. – polyphase NaCl-CaCl<sub>2</sub>-H<sub>2</sub>O and vapour-rich H<sub>2</sub>O-CO<sub>2</sub> inclusions. Greisenization formed at temperature of up to 500 °C (Ďurišová 1984).

2) "Alpine type mineralization" - 270-370 °C

Almost monomineral mineralization, formed by quartz or quartz-adularia-chloritemuscovite-calcite assemblage, contains  $H_2O-CO_2$  inclusions with about 5 mole % of  $CO_2$ . Homogenization temperatures range between 270 and 370 °C and salinity is mostly between 5 and 10 wt. % NaCl equiv. NaCl-KCl-CaCl<sub>2</sub>-MgCl<sub>2</sub> are the main components of the solution (Dobeš 2001).

3) Epithermal vein mineralization – 120-300 °C

The most common quartz  $\pm$  carbonate  $\pm$  fluorite  $\pm$  chlorite  $\pm$  prehnite mineralization type contains mostly aqueous fluid inclusions with homogenization temperatures ranging from 120 to 300 °C, variable salinity from 0.5 to 25 wt. % and variable composition of the solution: LiCl or NaCl  $\pm$  KCl  $\pm$  CaCl<sub>2</sub> $\pm$  MgCl<sub>2</sub> $\pm$  FeCl<sub>2</sub> (Dobeš et al., 2006).

4) Low-temperature calcite fracture fillings - 80-110 °C.

The late calcite mineralization was observed in the Jizera Granite along fractures with the indications of the late tectonic movement. The calcites revealed homogenization temperatures from 80 to 110 °C and salinity not exceeding 4 wt. % NaCl equiv.

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### 3D characteristics of pore space using X-ray microtomography

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X-ray computed microtomography is an experimental technique which can generate 3D images of internal pore space of investigated rock sample. It allows visualization and accurate quantitative measurements of spatial pore structure. Based on microtomography it is possible to obtain information regarding porosity e.g.: number of pore channels, their length, connections, pore network structure and their influence on permeability.

Roentgen computed microtomography (micro-CT) is a technique with wide application in many geological disciplines. Among important applications are measurements of porosity and fluid flow which are used in oil geology, rock mechanics and pedology.

One of the most important advantages of this method is its non-destructive character. This makes the technique useful for monitoring of active processes like water displacement and dissolved substances or water migration in sandstones during desaturation experiments. Micro-CT allows for the analysis of valuable and unique specimens like fossils or meteorites.

A large volume of literature presents micro-CT petrography abilities for magmatic and metamorphic rocks and for paleontology. Some papers show micro-CT application in structural geology for deformation experiments, documenting structure changes in 3 dimensions in time.

This year Oil and Gas Institute has purchased a roentgen microtomograph funded by the Ministry of Science and Higher Education. This microtomograph is one of the most modern devices with innovative architecture which allows obtaining a very high resolution images and customize samples size and speed of scanning.

This presentation shows the theoretical principles of roentgen microtomography, data acquisition process, pore space and mineral frame segmentation projection reconstructions and images rendering. Laboratory research results will be presented as images of internal microstructure of sandstones and limestones.

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## Transformations during spontaneous combustion of coal waste pile Kukla, Czech Republic

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The coal waste pile of Kukla mine in Oslavany (Czech Republic) was studied to characterize secondary minerals and their stability and to determine processes which influence the element outflow from this pile under temperate climate conditions. The pile burned from the late 19th century until the 1990's and has acquired a zoned nature, with original black material in the core of the pile, red material produced by burning close to the pile slopes, and grey and white efflorescent salts precipitated on the top and slopes of the pile. Three main stages of the formation of secondary minerals were found: (1) The oldest secondary mineralization, which was formed at high temperature stage during burning of the waste, consists of hematite, spinels, and corundum. At the same stage, native sulphur sublimated from hot gases near or at the surface of the pile. (2) Anhydrite, aragonite, calcite, and gypsum represent the minerals resulting from weathering of primary waste rock and also formed during cooling stage. (3) Hexahydrite, konyaite and picromerite are the youngest minerals in the pile, formed during late, low-temperature stage, by evaporation (Dokoupilová et al. 2006, 2007). The evolution of the formation of secondary minerals by evaporation follows the Hardie-Eugster evaporation model (Hardie and Eugster, 1970, in Drever, 1997).

Water leaching tests were used to evaluate the solubility of secondary minerals and release of elements. Evaporation of water was modeled by a geochemical program based on Pitzer's equations. A conceptual model of geochemical processes in the pile, which includes processes such as burning, weathering, and evaporation has been suggested.

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### Mineralogical and geochemical study of barite concretions from the Moravian part of the Carpathian Foredeep, Czech Republic – preliminary results

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Barite concretions occur at ten sites in the area between Brno and Znojmo. They are hosted by Lower Badenian silty and sandy calcareous clays (locally called "tegels"). Locally, barite nodules are associated also with gypsum crystals and concretions. The barite concretions are white, grey or yellowish and reach up to 15 cm in diameter and 2 kg in weight. The shapes are spherical or flattened, with botryoidal or smooth surface. The internal structure is variable. Most concretions are completely filled up having light, fine-grained core and fibrous rim. The core is occasionally cut by septarian cracks, completely filled by blocky yellow barite. Other nodules exhibit no growth zonation. Some concretions are empty, formed only by a thin barite crust.

Mineralogical study reveals barite as the only authigenic phase. Barite commonly contains Sr (0.07 to 1.35 wt. % SrO) and elevated Al (0.53 to 0.66 wt. %  $Al_2O_3$ ) and Na (0.09 to 0.17 wt. %  $Na_2O$ ; EPMA analyses). There is no systematic chemical evolution throughout the zonal concretions. The intergranular detrital phases include quartz, illite, muscovite, chlorite, calcite, feldspars, pyrite (replaced by gypsum) and dolomite. The concretions enclose also calcite fossil shells and/or wood. Bulk chemical analyses indicate that 4-20 wt. % of non-sulphatic phases are present.

The  $\delta^{34}$ S values vary between -11.2 and +27.4 ‰ CDT. The  $\delta^{18}$ O values range between +10.7 and +23.8 ‰ SMOW. There are no systematic isotopic trends across the concretions. In the  $\delta^{34}$ S- $\delta^{18}$ O plot, the data form two parallel positively correlated arrays. These data suggest (i) two-stage process of barite concretions formation in the Carpathian Foredeep, and (ii) mixing of two distinct sulphate sources: isotopically heavy residual sulphate from bacterial reduction of marine sulphate and isotopically light sulphate originating from oxidation of hydrogen sulphide (or pyrite) produced by the same process of bacterial reduction of marine sulphate. The primary source of barium may be found in detritus derived from the Brunovistulian basement (feldspars, post-Variscan vein barite mineralization).

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## Metamorphic and post-metamorphic fluids at the polymetallic Zn-Pb deposit Horní Město, Vrbno Group, Silesicum, Czech Republic

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The fluid inclusion and stable isotope study was conducted at the Horní Město Zn-Pb deposit, which is hosted by weakly metamorphosed Devonian paleotrachytes, paleorhyolites and sediments of the Vrbno Group. Samples include (i) stratiform polymetallic and barite mineralization, (ii) metamorphogenic quartz-calcite±dolomite± fluorite±sulphides segregation lenses parallel to schistosity of host rocks, and (iii) post-metamorphic veinlets cutting the foliation.

Two main types of metamorphic fluids were identified: 1) CO<sub>2</sub>-H<sub>2</sub>O-NaCl with low salinity (5–7 wt. % NaCl in aqueous solution), low content of CO<sub>2</sub> (2–7 mol. %) and homogenization temperatures ca. 200–300 °C, and 2) NaCl-MgCl<sub>2</sub>-H<sub>2</sub>O with low salinity (5–7 wt. % NaCl equiv.) and homogenization temperatures 120–220 °C. The position of isochores of both fluid types in PT-space agrees with predicted PT-estimate of Variscan metamorphic overprint in this area (350–400 °C, 4–5 kbars). The calculated highly positive fluid  $\delta^{18}$ O values around +10 ‰ SMOW are compatible with the metamorphogenic origin of fluids.

The clearly different fluid inclusion and stable isotope parameters showed samples from post-metamorphic veinlets. Their characteristic features include low homogenization temperatures (90–150 °C), high salinities (21–24 wt. % salts) and Ca-Na-Cl fluid composition. Most inclusions contain fluids rich in NaCl, however, examples with prevailing CaCl<sub>2</sub> were also documented. A similarity of temperatures derived from sulphur isotope thermometry and homogenization temperatures of fluid inclusions suggest a low-pressure formation conditions. The calculated fluid  $\delta^{18}$ O values around 0 ‰ SMOW indicate that the surface waters (meteoric or marine?) were predominating in the hydrothermal system. Their microthermometric and stable isotope characteristics are comparable to the post-Variscan brines that participated during formation of many types of barren and ore vein-type mineralizations along the whole eastern margin of the Bohemian massif, rather than to pure "metamorphogenic" fluids.

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### Age of regional metamorphism in the Karkonosze-Izera Terrane, Variscan Sudetes: a preliminary EMPA monazite study

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The timing of high-pressure metamorphism in the Variscan Sudetes (Sowie Góry and Orlica-Śnieżnik) is now well constrained with detailed monazite and Ar/Ar geochronologic results (Gordon et al. 2005; Schneider et al. 2006). The age of regional low pressure metamorphism preserved in the Karkonosze-Izera terrane is constrained primarily by Ar/Ar cooling age data on dominantly low-temperature micas (Marheine et al. 2002). In this study we employed the elemental electron microprobe analysis (EMPA) to obtain total-Pb monazite ages in an effort to constrain the timing of both regional (Variscan) metamorphism as well as determine the thermal effects of post-tectonic magmatism on the main metamorphic signature.

Fifteen samples of mica-schist from two transects were selected for the analyses. The northern transect is parallel to, but 10 km away from, the Karkonosze granite contact. The southern transect is perpendicular to the granite contact, beginning directly in the hornfels zone and extending to > 2 km south-east from the granite. The rocks consist predominately of medium grained, well-foliated, garnet-bearing mica schists with some garnets showing a rotated (i.e. syn-tectonic) paragenesis. Monazites form small laths (~15µm), mostly homogeneous, in a few samples low in Th and U. They occur dominantly in the matrix although some occur as inclusions in garnet.

Age calculations follow the protocol of Montel et al. 1996, modified by Konečný (2004). One hundred and twelve single spot analyses from five samples yielded a range of total-Pb dates from 428 Ma to 247 Ma, with single spot errors of  $\pm$  30 Ma. The main population of dates clusters at 327  $\pm$  6 Ma, which we interpret as the age of regional (dominantly greenschist) metamorphism of the Karkonosze country rock. The second largest age population of 365  $\pm$  6 Ma is consistent with the proposed age of high-pressure metamorphism of the nearby blueschist facies rocks. Surprisingly, the Karkonosze granite had little effect on the monazite ages.

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### Application of the sequential extraction procedure for speciation of selected heavy metals in airborne particulate matter

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Environmentally important processes, such as transport and bioavailability, are species dependent because different chemical species of elements have different physical and chemical properties. Despite of inherent analytical problems, selective extraction is one of the methods currently being used in metal speciation studies of soils, sludges and sediments. Still, the method is seldom used in environmental studies of airborne particulate matter.

On average, 60 g/m<sup>2</sup>/year of airborne particulate matter falls down in downtown Krakow. Although total concentration of metals in the dust is known from samples collected on the filters by monitoring stations, very little is known about metal speciation. The purpose of this research was to develop a selective sequential extraction method to identify the species of Zn, Pb, Cd, Ni, Fe and Mn in urban airborne solids. The underlying hypothesis is that speciation correlates with bioavailability of metals in question.

Four dust samples were collected from the roof of bus stops at different locations in Krakow. The modified Tessier's extraction procedure was used to chemically fractionate metals into: 1) "exchangeable", extracted with magnesium chloride solution; 2) "bound to carbonates", extracted with sodium acetate, adjusted to pH 5.0 with acetic acid; 3) "bound to iron and manganese oxides", extracted with hydroxylamine hydrochloride dissolved in acetic acid; 4) "bound to organic matter", extracted with hydrogen peroxide ( $H_2O_2$ ) at pH=2; 5) "residual", extracted with hydrofluoric and nitric acids.

About 90% of Mn, Zn, Cd and Pb are in the form of carbonates and/or bound to iron and manganese oxides (2<sup>nd</sup> and 3<sup>rd</sup> fractions). This means that they exhibit high environmentally mobile character which may also indicate their anthropogenic source. Fe and Ni were distributed more evenly between mobile and immobile species (about 30% in residual fraction). Based on the results obtained it was concluded that the application of the methodology in question provides chemical fractionation data that reflect the general sources and potential environmental hazards of the metals studied.

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### Comparative study of the Maksyutov and the Atbashi eclogiteglaucophane-schist complexes

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Comparison of the petrological, petrochemical and geochemical features of the Maksyutov (Southern Ural) and the Atbashi (Southern Tien-Shan) eclogite-glaucophaneschist complexes was carried out to obtain additional evidence on the suggested protolith composition and to determine their affiliation to different geodynamic terrains within the Ural-Mongolia Fold Belt. Some geochemical regularities were identified based on the chemical composition of eclogites and associated glaucophane-schist rocks. Major, trace, and REE elements were also used as indicators of either magmatic or metamorphic origin of the eclogite bodies (lenses, layers, etc.) within the eclogite-glaucophane-schist complexes.

Both, the Maksyutov outer and the Atbashi inner complexes were generally formed during a single global event - the Hercynian Orogeny. Based on the geochemical data, it is assumed that the deeper occurring Maksyutov eclogite-glaucophane-schist complex was formed in the trough-like structure on the border between the Eastern-European Platform (paleo-continent) and the Eastern Urals Slope (paleo-ocean). The least altered eclogite samples of the Maksyutov terrain were formed perhaps from the tholeiitic basalts (between the E-MORB basalt and the Island Arc basalt). The hypothesis of magmatic origin of the Maksyutov eclogites seems to be more preferable than the model of the descent of the Earth crust terrain. This idea is supported by physicochemical modeling of its formation (MELTS program) and by geochemical and mineralogical evidences: by abnormally high titanium content in the rocks of the complex, cerium positive anomaly on the REE spectrums, prevalence of the LREE in the Maksyutov rocks, higher content of the REE in these rocks than in the Atbashi eclogites.

Plagioclase stability on the MELTS modeling diagram obtained for the Atbashi eclogites (as opposed to KFsp for the Maksyutov protolith) and a prominent negative Euanomaly in the REE spectra contradict the hypothesis of the magmatic origin of the Atbashi complex. So, it seems to be the Atbashi eclogites most likely has metamorphic origin at a relatively shallow depth (30-35 km).

The extensive studies of clinopyroxenes from both, Maksyutov and Atbashi eclogites by X-ray powder diffraction and Mössbauer spectroscopy revealed several structural modifications in the Cpx phase (Jd-Aeg-Di solid solution), which have different elastic properties (the unit cell volume and the  $\beta$ -angle). More detailed information was obtained on the local structure of these modifications. The studied omphacites have the perfect structure, characterized by local cation ordering in M1 and M2 sites (apparently, sp. gr. P2/n), which perhaps could be held true under changing metamorphic conditions and used

as indicator of them. These results may be used also to correct clinopyroxene thermodynamic data applied to thermobarometry.

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### Minerals of the rosasite-zincrosasite series from the Andrássy-I. mine, Rudabánya, Hungary: The zincrosasite problem

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Minerals of rosasite-zincrosasite series have been found in the fissures of limonite ore of the Andrássy-I. mine (Rudabánya). They form turquoise blue to very pale blue, nearly colourless or pale green globular aggregates up to 0.5 mm in diameter, as well as botryoidal encrustations associated with malachite, brochantite, cerussite, aurichalcite and goethite (Szakáll et al., 2001). Rosasite and zincrosasite are secondary minerals. They are alteration products of primary sulphides (e.g. chalcopyrite, bornite, chalcocite, sphalerite).

Zincrosasite from Tsumeb, Namibia, was first described by Strunz (1959) as (Zn,  $Cu_2(CO_3)(OH)_2$  with atomic ratio Zn:Cu = 58.60:51.94 or greater. Therefore, this is a zincdominant analogue of rosasite (Cu, Zn)<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>2</sub>. The original description of zincrosasite is very brief (only six sentences) and we could not find any additional mineralogical data about it in the literature (see e.g. Anthony et al., 2003).

The structural formula of the minerals of the malachite-rosasite group is Me1Me2(CO<sub>3</sub>)(OH)<sub>2</sub>, where Me1 and Me2 are metal cations in octahedral coordination. According to the present nomenclature Me1 = Cu and Me2 = Cu in malachite, and Me1 = Cu and Me2 = Zn in both rosasite and zincrosasite, but Cu > Zn in rosasite and Cu < Zn in zincrosasite. However, this distinction between the two later species is incorrect according to the IMA rules, and the redefinition of zincrosasite is necessary as  $Zn_2(CO_3)(OH)_2$ .

The results of chemical analyses of zincrosasite could not be found in the literature (Anthony et al., 2003). For the first time, the results of microprobe analysis of zincrosasite is presented herein (a specimen from the Andrássy-I. mine, in weight per cent): ZnO 52.80, FeO 0.42, CuO 16.01, SO<sub>3</sub> 0.20, Sb<sub>2</sub>O<sub>3</sub> 0.01, CO<sub>2</sub> (calc.) 18.84, H<sub>2</sub>O (calc.) 7.71, total 95.99, which corresponds to  $(Zn_{0.52}Cu_{0.47}Fe_{0.01})_{\Sigma=1.00}$  Zn<sub>1.00</sub>(CO<sub>3</sub>)(OH)<sub>2</sub>. This specimen appears to be suitable for the redefinition of zincrosasite.

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#### Dissolution of vanadinite at pH= 2.0-6.0 and 25°C

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Vanadinite  $Pb_5(VO_4)_3Cl$ , along with pyromorphite  $Pb_5(PO_4)_3Cl$  and mimetite  $Pb_5(AsO_4)_3Cl$ , belong to the ternary system of lead apatites. The anionic isomorphic substitutions of  $PO_4^{3^-}$ ,  $VO_4^{3^-}$ ,  $AsO_4^{3^-}$  are ubiquitous among these minerals. The continuity of pyromorphite-mimetite-vanadinite solid solution series has recently been confirmed. Pyromorphite, mimetite and their solid solutions exhibit relatively high thermodynamic stability in the environment. However, thermodynamic properties of vanadinite and its anionic solid solutions with other lead apatites are poorly known. This limits understanding of the mechanisms of anionic substitutions among lead apatites, which is necessary to determine the effect of substitution on their formation and transformations.

Dissolution of synthetic vanadinite at 25°C has been carried on in batch experiments for 5 months at pH equal to 2.0, 2.5, 3.0, 3.5, 4.0, 5.0 and 6.0. Solutions were periodically syringe sampled, and Pb(II), V(V) and Cl concentrations were measured. The system was considered to be in equilibrium when the results of consecutive analyses were equal within two standard deviations of triplicate experiments. The solutions with the initial pH≥4.0 reached the equilibrium within two months. The Pb(II) concentration totalled 6 ±0.2  $\Box$  mol/dm<sup>3</sup> for initial pH=4.0, and below 4 µmol/dm<sup>3</sup> for pH=5.0 and 6.0. Solubility of vanadinite increases with decreasing pH but final concentration of Pb(II) didn't exceed 0.7 mmol/dm<sup>3</sup> in any of the experiments. At the conditions of experiment, dissolution of vanadinite appears to be incongruent: a decrease in Pb/Cl ratio over time was observed. This indicates precipitation of a mineral phase different from Pb<sub>5</sub>(VO<sub>4</sub>)<sub>3</sub>Cl during the dissolution. A newly formed phase was investigated with scanning electron microscopy (SEM/EDS). Based on morphology and element composition, the precipitated phase was identified as chervetite (Pb<sub>2</sub>V<sub>2</sub>O<sub>7</sub>). The results allow supplementing the thermodynamic databases used for computer modeling of geochemical reactions. This provides the foundation necessary for further investigation of the thermodynamic stability as well the mechanisms of formation and transformations of vanadinite.

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# Ore minerals from the dolomitic veins in the serpentinite rocks of the Letovice Crystalline Complex (Czech Republic)

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Minerals found in dolomite veins cutting serpentine rocks around Letovice and its surroundings composed remarkably heterogeneous set which is different from any other locality in the Bohemian Massif. The composition of copper minerals (bornite, chalcocite, covellite, chalcopyrite), millerite, dolomite veins and magnetite is similar to the composition of their host ultrabasic rocks. Lead and bismuth (galena, native Bi) are considered in this environment as atypical. Parkerite and wittichenite are transitional – they consist of elements of both groups. Despite being impossible to determine detailed order of crystallization, it was implied by microscopic studies that sulphides Pb-Bi(Cu) are relatively older than copper minerals. Fe-Cr spinelides that are rarely found in dolomite veins on the outline of serpentine rock are possibly relicts of pre-metamorphic magmatic stage. The formation of "ribbon-like" pure magnetite in the immediate vicinity of sulphides is probably related to redeposition processes of older stages in process of hydrothermal alteration. Chondrite normalized REE pattern of dolomite shows positive Eu anomaly and relatively elevated content of HREE.

The isotopic composition of sulphur of hydrothermal fluids ( $\delta^{34}S = +4 a \pm +5 \%$  CDT) indicates that sulphur was not derived from meta-ultrabasic rocks. Calculated  $\delta^{18}O$  value of hydrothermal fluids is +3 to +5 ‰ SMOW (temperatures 188-238 °C, i.e. temperatures of homogenisation of primary fluid inclusions); calculated  $\delta^{13}C$  value of hydrothermal fluids is -5 to -6 ‰ PDB. On the formation of Pb-Bi minerals the temperature could be higher (approx. 250 to 300 °C). Secondary fluid inclusions in dolomite contain methane, primary fluid inclusions are relatively high in salinity (17.0 to 20.9 wt.% NaCl equiv.). Such parameters correspond mainly to brine derived from a sedimentary basin. The substance of metals was probably extracted during migration of solutions from its surroundings.

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### Mobilization of Cu by rain fall on a historical copper mine dump, L'ubietová, Slovak Republic

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Historical mine waste dumps in Ľubietová are well known to mineral collectors as a type locality of copper mineral libethenite. The objective of this study was identification and modeling of geochemical processes mobilizing Cu by waters percolating though piles of copper ore dumps. Samples of water from a spring and a small stream coming out of the tailings show that the concentrations of major components Ca, Mg, Na and K are relatively low, equal to 5.83, 6.83, 2.73, and 1.96 mg/L, respectively. The major anions are SO<sub>4</sub><sup>2-</sup> (33.12 mg/L) and HCO<sub>3</sub><sup>-</sup> (28.07 mg/L). The Cu concentration is relatively high: close to the spring it equals to 2.0 mg/L and decreases down the stream to 0.9 mg/L (200m from the spring).

The bottom of a stream coming out from the tailing is covered by green earthy precipitate. It covers rocks, leaves and all the objects with tight coating. X-ray diffraction analysis indicates that it is amorphous. The major component of the coating is organic (probably algae) and can be removed with  $H_2O_2$ . Scanning electron microscopy microanalysis (SEM/EDS) shows the presence of Cu and P. More research is needed to explain the character and mechanisms of formation of this coating.

Primary copper minerals (e.g. chalcopyrite, tetrahedrite) and secondary copper minerals (malachite, langite, azurite, libethenite, reichenbachite, and covellite) were identified in the deposit. Optical microscopy reveals that the secondary copper minerals are a result of transformation of chalcopyrite. Hydrochemical modeling using PHREEQC computer code confirms that chalcopyrite exposed to rain water and air is thermodynamically unstable. This can contribute to increased concentration of Cu in waters. Also, formation of secondary langite and covellite, determined by optical microscopy and SEM/EDS, is consistent with PHREEQC calculated saturation indices. The same applies to Fe precipitation as goethite and lepidocrocite, which is consistent with hydrochemical modeling.

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### Pb-(AI,Fe<sup>3+</sup>) - arsenate association from Rędziny, Rudawy Janowickie, Southwestern Poland

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The deposit of dolomitic marbles at Rędziny, located in the Kowary-Czarnów Unit, occurs within the Eastern metamorphic cover of the Karkonosze granite. The proximity of the granite gave rise to the formation of an abundant, polymetallic, hydrothermal minerals in dolomites, and during weathering caused development of secondary mineral assemblages (arsenates, vanadates, phosphates, carbonates and oxides; e.g. Parafiniuk, Domańska 2002; Gołębiowska 2003; Gołębiowska et al. 2006).

Philipsbornite and segnitite, the Pb-(Al,Fe<sup>3+</sup>)-dominant arsenate minerals within the alunite-jarosite family, are very rare secondary phases found in the oxidation zone of ore deposits. Carminite, other Pb-Fe-arsenate, co-existing with both previously mentioned minerals, is more common in nature. To date however, these minerals have not been found in Poland. In Rędziny, Pb-(Al,Fe)-arsenates were identified in small cavern (up to 3-4mm), or in microareas, within accumulation of arsenopyrite and sphalerite, Ag-bearing galena, Cu(Ag)-Pb-Bi(Sb) sulphosalts and chalcopyrite.

The XRD, SEM coupled with EBSD and EDS, and chemical investigations (by means of WDS method) were carried out to characterize these phases. The analyses were calculated on the basis of 14 O apfu for philipsbornite-segnitite and on the basis of 10 O apfu for carminite. The mean empirical formula for philipsbornite is:  $(Pb_{0.90}Bi_{0.12}Ca_{0.04})$   $(Al_{2.30}Fe_{0.62}Cu_{0.01}Zn_{0.01})[(As_{0.89}P_{0.09}S_{0.02})O_4/(As_{0.89}P_{0.09}S_{0.01})O_{3.03}(OH)_{0.97}](OH)_{6.00}$  (n=30), and for segnitite:  $(Pb_{0.90}Bi_{0.04}Ca_{0.05}K_{0.06})(Fe_{2.27}Al_{0.72}Cu_{0.01}Zn_{0.03})[(As_{0.88}P_{0.01}S_{0.06})O_{3.85}(OH)_{0.15}/(As_{0.88}P_{0.01}S_{0.06})O_3(OH)_{1.00}](OH)_{6.00}$  (n=10). The empirical formula of carminite is:  $(Pb_{1.01}Bi_{0.01}Ca_{0.05})(Fe_{1.78}Al_{0.13}Cu_{0.01})[(As_{0.99}P_{0.01})O_4/(As_{0.99}P_{0.01})O_{3.93}(OH)_{0.07}]$   $(OH)_{2.00}$  (n=25). The presence of Pb-(Al,Fe)-arsenates within one of the deepest exploitation horizons, and within weakly altered polymetallic mineralization suggests formation of the aforementioned phases during initial weathering stage.

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## Berryite, a Cu-Ag-Pb-Bi sulphosalt from Rędziny; Rudawy Janowickie, Southwestern Poland

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Ore mineralization in the Rędziny area (Rudawy Janowickie Mts) is associated with schists and amphibolites of the Kowary-Czarnów Unit that borders the eastern margin of the Karkonosze granite intrusion. The main minerals arsenopyrite and cassiterite are accompanied by various base-metal sulphides and sulphosalts. Primary sulphide mineralization has been affected by hipergenic alteration, resulting in a wealth of secondary minerals (Gołębiowska 2003; Gołębiowska et al. 2006; Parafiniuk, Domańska 2002). This paper presents mineralogical characteristic of berryite, a rare Cu-Ag-Pb-Bi sulphosalt.

Berryite, Ag<sub>2</sub>Cu<sub>3</sub>Pb<sub>3</sub>Bi<sub>7</sub>S<sub>16</sub>, occurs within arsenopyrite veins in the form of very thin tabular, elongated crystals up to 100µm long, together with giessenite, (Ag,Cu)-bearing cosalite, mineral of the aikinite-bismuthinite series, Ag-bearing galena and gustavite. Small irregular inclusions of berryite in this association have been rarely observed. Grains of berryite commonly occur between large grains of coexisting minerals, very often also in outer rims around these aggregates. The calculated composition of berryite on the basis of  $\Sigma Me = 15$  apfu is (Ag<sub>2.04</sub>Cu<sub>2.85</sub>Fe<sub>0.02</sub>Mn<sub>0.01</sub>Cd<sub>0.01</sub>)Pb<sub>3.01</sub>(Bi<sub>7.03</sub>Sb<sub>0.03</sub>) S<sub>15.86</sub>Se<sub>0.04</sub> (n = 88). The Cu/Ag ratio varying in the narrow range from 1.39 to 1.52, and minor Sb substitution for Bi correspond to berryite from other occurrences.

Thermochemical conditions of crystallization of the Ag-bearing sulphosalts from Rędziny have been evaluated by Pieczka *et al.* (2005). Berryite occurring in the polymineral aggregates of sulphosalts probably crystallized within the temperature range of 350-320°C.

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# Opal breccia from Dobrica Hill (Central Slovakia): a mineralogical and geochemical study

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The occurrence of opals at Dobrica Hill (Central Slovakia) is connected to Sarmatian volcanic rocks which consist of altered andesites and overlying fresh pyroclastic rocks. The low hydrothermal activity is documented by presence of carbonates, chalcedony and opal (Karolus & Karolusová in Harčár, 1988). The opal specimens were studied using XRD, FT-IR, Raman spectroscopy, and EMPA methods. Macroscopically, all 5 samples are characteristic with well observable breccia texture and white to yellow white patina. Rarely the fragments of fossils were determined on the surface. Clasts are deep green, whereas the infilling between the clasts is mainly light green. According to the XRD analysis, the clasts and the infilling consist of pure opal-CT with variable ordering. Plagioclase, clinopyroxene, jarosite and goethite have been identified with Raman and FT-IR spectroscopy. In thin sections, the clasts and infilling show low birefringence characteristic for opal-CT. Jarosite occurs as irregular crystals, frequently grouped into the aggregates or occasionally as euhedral rhombohedral crystals. Since the opal-CT doesn't have crystalline structure; (only long range ordering has been reported), it is impossible to calculate its stoichiometric formula. Therefore, the results from chemical analysis using EMPA method are given in the weight percents. The opal-CT clasts are enriched in Al<sub>2</sub>O<sub>3</sub> (1, 2 - 2, 2, wt) and FeO<sub>TOT</sub> (0,7 - 1,2 wt%), CaO (0,1 - 0,4 wt%), MgO (0,3 - 0,5 wt%). Infilling is depleted in Al<sub>2</sub>O<sub>3</sub> (0 - 1, 1 wt%), FeO<sub>TOT</sub> (0, 0 - 0, 7 wt%), CaO (0, 0 - 0, 2 wt%), MgO (0, 0 - 0, 2 wt%) but the content of SiO<sub>2</sub> (91,7 - 100,5 wt%) is higher than in opal-CT clasts (87,3 - 93,9 wt%). The origin of opals is connected with hydrothermal activity. However, the origin of the opal breccia is more complex. The presence of fossils fragments suggests that the hydrothermal solutions intruded into the basin with seawater leading to polymerization of  $H_4SiO_4$ . Due to the aging the newly formed opal cracked. Consequently, the opal layers were covered with the pyroclastic material and reheated. This resulted in remobilisation of  $SiO_2$  which filled the cracks between the clasts forming the well observable breccia textur.

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#### Mineralogy of Noctis Labyrinthus (Valles Marineris, Mars) - results from imaging and Fourier spectrometers

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The data of the OMEGA imaging spectrometer and the Planetary Fourier Spectrometer (PFS) of the Mars Express mission have been used to analyse the diversification of the mineral composition of the Noctis Labyrinthus region, a complex pattern of intersecting fault systems, which is situated in the western end of the Valles Marineris canyon on Mars.

Dominant minerals of the Noctis Labyrinthus area are pyroxenes and plagioclases, which are present both on the canyon floors and plates. Presence of clinopyroxenes is observed both in the central and western part of Noctis Labyrinthus. Plagioclases are located mainly in the central part. Phyllosilicates (e.g. monmorillonite, nontronite) are observed on the slopes and floors of canyons in the western and eastern part of Noctis Labyrinthus. Large quantity of hematite covers the plates, mainly in the western part of the study area. In the central part small quantities of sulfides (chalcopyrite, arsenopyrite) coexist in the hollows. Very small quantities of goethite and lepidocrocite are also present on the slopes. Presence of phyllosilicates in the oldest part of rock basement and large quantity of hematite on the plates corresponds to the stratigraphy of Mars, which has been advanced by the OMEGA team on the basis of the global mineral composition of the surface.

In a part of spectra from both OMEGA and PFS spectrometers absorption bands show reduced intensity (contrast) in relation to the library spectra. It could be the reflection of different grain sizes of the materials. In the case of goethite and lepidocrocite the difference in the intensity of the bands might be caused by the -OH group content (less hydrated variety of mineral). Test comparison of the OMEGA spectra of the investigated area and the spectra of rocks from JHU Spectral Library indicates basaltic andesite.

In the case of the Noctis Labyrinthus region the quality of the data set collected by OMEGA and PFS is handicapped by a considerable distance of the spacecraft from pericentre during measurements and an increased thickness of the atmospheric column arising from the few-kilometers deep grabens making the significant part of the explored area. The PFS data could be additionally affected by the presence of the dust signatures in the analysed spectra.

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## Two stage evolution of niobian titanite from hedenbergite vein skarn at Písek, Moldanubian Zone, Bohemian Massif

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Hedenbergite skarn with accessory niobian titanite occurs in marble at the Kamenné doly quarry near Písek (Czech Republic). Small layers and xenoliths of calcite-chondroditephlogopite marble are hosted in leucocratic biotite migmatites with numerous intrusive bodies of ultrapotassic melagranite to quartz syenite (durbachite). Marbles are locally rimmed with a zone, up to 2 m thick, formed by a massive pyroxene-garnet-vesuvianite and pyroxene-quartz skarns (Houzar et al. 2008). Zoned veins of hedenbergite skarn are up to 3 cm thick and cut discordantly marble close to its contact with massive garnet-pyroxene and pyroxene skarn. They consist of hedenbergite (Hd<sub>53-81</sub>Di<sub>15-43</sub>Jh<sub>3-5</sub>) and minor quartz, clinozoisite, calcite, altered Ca-plagioclase, scheelite and sulphides. Grains of niobian titanite, typically enclosed in hedenbergite and quartz, are concentrated in central part of skarn veins.

Niobian titanite exhibits complex zoning in BSE. The individual zones and the individual compositional subtypes distinguished in niobian titanite gave rather distinct compositional evolution and substitution exchange vectors. Negative correlations (Al,Fe)+F vs.  $R^{4+}$  and (Al,Fe)+(Nb<sup>5+</sup>,Ta<sup>5+</sup>) vs.  $R^{4+}$ , where  $R^{4+} = Ti$ , Sn and Zr, and low contents of Na in niobian titanite correspond to the heterovalent substitutions: (1) (Al,Fe)(Nb,Ta)Ti<sub>-2</sub> dominant in Nb-rich titanite and Nb-moderate titanite of the central zone and (2) Al(F,OH) (TiO)<sub>-1</sub> typical for Nb-poor, Al,F-rich titanite of the outer zone. Textural relations of niobian titanite and crystal structural constraints indicate two stages of evolution. The first stage - formation of heterogeneous Nb-rich to Nb-moderate titanite of central zone with dominant substitution (1) and only minor participation of the substitution (2) – represents a primary crystallization from relatively high-temperature fluids. During the second stage, alteration of less heterogeneous Nb-poor, Sn-enriched and Nb-poor, Al,F-rich titanite of outer zone, Al,F-rich titanite of outer zone, Al,F-rich titanite induced by F-rich fluids took place, and resulted in formation of less heterogeneous Nb-poor, Sn-enriched and Nb-poor, Al,F-rich titanite of outer zone with dominant substitution (2).

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## Compositional variation of amphibole from metabasites of the Sowia Valley, Izera-Karkonosze Block (West Sudetes)

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On the SE side of the metamorphic cover of the Karkonosze granite and within metapelites of the Sowia Valley crop out several bodies of moderately foliated porphyroblastic metabasites. In these rocks amphibole appears both as porphyroblasts and prisms parallel to the metamorphic foliation plane. Additionally, well-foliated metabasites (amphibole schists) devoid of porphyroblasts were also found. Depending on the microtextural position of amphibole crystals in the rock, different core-to-rim chemical variation trends have been ascertained. The porphyroblast and prisms oblique to the main foliation in amphibole schist show zoning corresponding to a compositional shift from Mg-hornblende to tschermakite and then to Mg-hornblende (or actinolite) field. The amphiboles from matrix and those from pressure shadows around porphyroblasts are tschermakite in cores and actinolite at rims. In one sample of schist, the zoned blasts of amphibole are overgrown by late-to post-tectonic cummingtonite.

Based on these observations, detailed thermobarometric estimations involving amphibole end-member equilibria enabled the unravelling of the metamorphic evolution of the metabasites studied. Peak metamorphic conditions (M<sub>2</sub>) of 620°C and 5.5-6 kbar were preceded by the variously recorded M<sub>1</sub> stage (T: 460-540°C, P: 2.6-5.0 kbar), while the last metamorphic episode (M<sub>3</sub>) took place at 450°C and 2.5 kbar and was recorded by the samples collected in the proximity of the Karkonosze pluton. The cummingtonite-bearing sample of amphibole schist recorded two stages of metamorphism (450°C, 2.3 kbar  $\Rightarrow$  520°C, 4 kbar).

The amphiboles studied shed a light on polystage metamorphism of the Sowia Valley metabasites. Two first stages of MP-MT metamorphism, roughly coeval with deformation events, took place under the epidote-amphibolite then amphibolite facies conditions, whereasthe last stage  $M_3$  was linked with retrograde metamorphism. Due to onset of thermal activity of the Karkonosze granite, this relatively LP-HT metamorphism is well detectable in metabasites located closer to the Karkonosze granite, as the re-equilibration of mineral assemblages and eventually growth of cummingtonite took place.

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## Metabasic rocks from the Polish part of the Orlickie Mts.: preliminary result of a geochemical study

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Metabasites of the Polish part of the Orlickie Mts. form several outcrops of variously foliated, fine- to coarse-grained (sometimes porphyroblastic) rocks composed of amphibole, plagioclase and subordinate chlorite, ilmenite, rutile, garnet, epidote, apatite and quartz. Mostly well-defined trends between major elements and Mg# (Mg#: 58-67) and linear correlations between pairs of HFSE indicate that primary concentrations of elements were not disturbed during metamorphism. Geochemically these rocks are classified as Sisaturated (ol- and hy-normative) basalts and trachybasalts of tholeiitic affinity. Several discrimination diagrams reveal that their chemical features are typical of within-plate basalts ranging from E-MORB to N-MORB. The chondrite-normalised REE patterns show variable enrichment/depletion in LREE ([La/Yb]<sub>CN</sub>: 0.49-2.26) resulting in gradual change of slope of diagram lines from positive to negative one; sometimes positive Eu anomaly is observed. These diagrams also display fairly flat profiles and weak fractionation of HREE ([Tb/Yb]<sub>CN</sub>: av. 1.3±0.1). When compared to primitive mantle (PM), the metabasites studied display moderate enrichment in incompatible elements (9-20 x PM) and systematic decrease of concentration from LREE towards least incompatible elements, varying concentrations of LILE and only slight negative Nb, Ti and P anomaly. In general, profiles follow that of E-MORB yet displaced towards higher abundances relative PM. Few samples show depletion in most incompatible elements: their diagram lines resemble either that of N-MORB or intermediate between E- and N-MORB.

Several geochemical features indicate that variation of chemical composition is most likely attributable to different degrees of partial melting coupled with source heterogeneity (variously depleted asthenospheric mantle). There is no evidence for introduction of metasomatic component into the source, while crustal contamination effects are mostly negligible. Melt was generated at shallow levels within spinel (±garnet) stability field at depths probably not exceeding *ca* 60 km.

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# Lower Cretaceous "black smoker" chimneys in pillow basalt beds in the Eastern-Mecsek Mts.

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The goethitic iron ore formation near Zengővárkony is known as "Lahn-Dill"-type mineralisation, but the origin of the iron ore is well debated till now. Although none of the specialists have published about sulfides from this ore, well developed sulfide chimneys were found in these pillow-basalt. and there are other evidence indicating that the Zengővárkony iron ore district was a "black smoker" like area at the late jurassic-early cretaceous period.

The presence of hyaloclastite and peperite at the edge of these pillow-basalt beds suggests that these rocks are non piroclastic, which is contradictory to some previous publications (*Pantó*, 1955; *Csalagovits*, 1960; etc.). The inner parts of basalt is composed of various size pillows with "chill margins" (the average diameter of pillows is 1-2 m). The pillows core, barely altered, often consists of: Ti-augite and labradoritic plagioclase phenocrists, opaque minerals (ilmenite, magnetite, pyrite), and secondary minerals (nontronite, goethite, calcite, quartz). The texture is variolitic. The cavities, filled with nontronite and calcite, sometimes quartz, are from mm to cm in size. Metasomatized calcareous mud with hydrothermal cavities can be found between the pillows which was interpreted by some authors as limestone xenolithes.

All pillow beds contain cracs, few milimeters in width. Within centimeters from these cracks the rock, usually purple, turns brown. Some of the meeting points of these cracks developed chimney structures near the surfaces of "chill margins" of the pillow basalt. One of these chimney systems is 1 m high and 1 m wide. The top of this chimney system metasomatized calcareous mud can be found. The chimney system consists of individual pyrite and marcasite tubes, few milimeters wide, having concentric layers. The inner parts contain  $40 - 60 \,\mu$ m pyrite framboids. The individual hexagonal pyrite crystals are about 2-3  $\mu$ m in size. The marks related to the bacterial activity can be found within the sulfides. They form branching lines, few micrometers in size, with sulfides oxidized to iron oxides and sulfates. The external rims of the tubes are made of acicular calcite and the last to precipitat was quartz. As a summary, partly the goethitic ore deposit could have been sulfides.

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#### Chronological constraints on the provenance and depositional ages of the supracrustal rocks of the Orlica-Śnieżnik Dome, West Sudetes

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Two supracrustal formations have been traditionally distinguished in the Orlica-Śnieznik Dome (OSD): the Młynowiec Fm., which has been supposed to represent an older, Middle Proterozoic sedimentary succession and the Stronie- Fm. that could represent a subsequent Lower Paleozoic depositional event. Rocks of these formations are separated by an extended horizon of light quartzites that are considered to be metamorphosed basal conglomerates of the Stronie Fm. (Don et al. 2003). In order to examine possible differences in maximum depositional ages and provenances of these rocks, the SHRIMP detritial-zircons geochronology have been performed on (1) paragneisses of the Młynowiec Fm., (2) light quartzites and (3) mica schists of the Stronie Fm. The studied metasediments (altogether 45 spots in each sample were analyzed) contain comparable zircon age spectra, which strongly suggest that detritial components of the Młynowiec Fm., the light quartzites and mica schists of the Stronie Fm. originated from the same source area. The microprobe dating has provided evidence for Archean (2.5-2.8) Early Proterozoic (2.1-1.8 Ga) and Late Proterozoic (660-640 Ma, 610-590 Ma and 570-530 Ma) geologic events, which indicates the connection of the OSD with the West African cratonic province. Presence of ca. 530 Ma old zircons in the Młynowiec Fm, indicates that its maximum depositional age is not Proterozoic, as it was assumed, but Early Cambrian. In addition, in order to specify the age of the Stronie Fm., 30 spots within 25 zircons grains from metabasites of Mt. Krzyżnik region were analyzed. These rocks, which plausibly represent lava flows deposited together with adjacent carbonate rocks, contain Paleoarchean (3.3 Ga), Early Proterozoic (2.1-1.9), Late Proterozoic and Cambrian U-Pb zircon ages. 8 analytical points defining the Neoproterozoic age cluster gave the concordia age of 599+/-18 Ma, whereas 14 points obtained from both internal and outer parts of magmatic zircon grains gave the age of 489+/-11 Ma. The most plausible interpretation of the obtained results is that the studied metavolcanic rocks originated from melting of the existing continental Cadomian crust at ca. 500 Ma. In conclusion, new U-Pb SHRIMP dating show that protholits of the Młynowiec and Stronie Fms. i.e. tuffs and lavas together with pelitic and carbonate rocks, represent single Late Cambrian sedimentary succession, which had deposited on the Neoproterozoic crust. The obtained age of the supracrustal rocks indicates a very short period of time between their sedimentation and a possible deformational event which was terminated by Early Paleozoic granitic intrusions.

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#### Electrochemical copper cementation at the Podlipa dump-field, L'ubietová deposit (Slovakia)

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The surrounding of the Ľubietová belongs from the historic viewpoint to the most important ore regions of Slovakia. The hydrothermal copper mineralization of this region is developed within three occurrences: Podlipa, Svätodušná and Kolba. In addition to Cu and Fe also Co, Ag and Ni mineralization is important. All these occurrences (but above all Podlipa) were exploited from the prehistoric times. Approximately 25 thousand tons of copper was exploited during 500 years (Bergfest, 1951). Ore mineralization is represented mostly by chalcopyrite, less by tetrahedrite and pyrite. In the quartz gangue mineralization also siderite and ankerite is present.

The samples of the surface water from the reference area, drainage water at the dumpfield as well as of the groundwater were analysed by AAS. Contamination by Cu, Pb, Zn, Cd, As, Sb, Fe, Ni, Co was studied. The Cu content in the surface water from the reference area ranges from 0.0173 to 0.0211 mg. $\Gamma^1$ . In contaminated water from the depression at the foot of the dump-field it varies from 1.81 to 2.06 mg. $\Gamma^1$ , and in the sediments of above mentioned depression it reaches 15 402 ppm Cu, 134 ppm Pb and 220 ppm As.

Cementation is a electrochemical process ("internal electrolysis") of crowd-out effect of metals based on electrochemical reaction between the cementator-metal and ions of precipitating metal. Steel nails immersed in the cementation water of the depression beneath the dump-field were oxidized within a month and their surface was covered by layer of green coating, containing of Cu secondary minerals and of cementation copper. Optical study of polished sections and the study by electron microprobe proved gradual precipitation of copper. The cementation copper is of a high fineness. The electron microprobe point analyses revealed Cu contents of up to 96.07 wt.%.

The ability of the drainage water to precipitate cementation copper on the iron surface gives the possibility to realize Fe-barrier for elimination of heavy metals from the drainage water and contributes to the remediation of the mining district.

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# Bismuth minerals from Banská Štiavnica and Hodruša epithermal gold-silver-base metal deposits

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The epithermal base and precious metal mineralization is situated in the large Banská Štiavnica-Hodruša ore district. Vein system is localised in the central part of the Štiavnica stratovolcano. The characteristic vertical zoning could be observed with increase of depth: Au-Ag, Pb-Zn and Cu zone. Cu zone occurs as elevated Cu-content in the Rozália and Bieber veins only. The presence of Bi minerals, typical for the deeper parts of the vein system, is associated with higher contents of chalcopyrite, bornite, scheelite and hematite. Hodrushite is a typomorphic mineral for the Rozalia vein (Koděra et al. 1970). Together with aikinite, wittichenite (sometimes Ag bearing) and emplectite it is the most common Bi sulphosalt in the quartz-hematite-chalcopyrite aggregates. The gold of higher fineness (860-910) associates with Bi minerals: emplectite, matildite, hodrushite and paděraite. The various Bi sulphosalts are characteristic for the upper part of the Rozalia vein. The sulphosalts of the cuprobismutite homologous series (kupčíkite - Fe rich, hodrushite - Ag, Pb and Fe bearing, cuprobismutite - Ag and Pb rich), bismuthinite derivatives (bismuthinite, gladite, krupkaite, hammarite, lindströmite friedrichite, aikinite), Cu bearing minerals of the pavonite homologous series (pavonite, makovickyite, benjaminite and N=6) together with berryite (Ag rich), paděraite (Ag, Pb bearing) and emplectite occur there. The Ag-Cu-Pb-Bi minerals of the lillianite homologous series (vikingite, ouravite) together with minerals of the galena-matildite solid solution occur in the deeper part of the Bieber (500-700 m deep) and Rozalia veins (300-400 m deep). These minerals crystallised under the higher temperature conditions in the copper mineralization. Higher temperature could be demonstrated by presence of the myrmekitic intergrowth of the galena and matildite. Sometimes the minerals of the tetrahedrite-freibergite series, polybasite, pearceite with small Bi content occur in these aggregates. Members of the stibioluzonite-luzonite series with various Sb/(Sb+As) ratios were also identified.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



## HCNOS stable isotopes for environmental reconstructions: why most of the up to the date models have to be revised

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Various components of freshwater sediments especially carbonates, sulphates, silica, organic matter, peat and tree rings are potentially abundant archive to reconstruct past environmental conditions including climates. However, it is not clear in what extend (from dominant to negligible role) isotopic composition of these components is determined by: (i) temperature, (ii) physiology of the living plants (various species fractionate differently), (3) isotopic composition of assimilated compounds e.g.  $CO_2$ ,  $SO_x$  and  $H_2O$ , (iv) isotopic fractionation resulted from assimilation and respiration, (v) pH, Eh, (vi) kinetics and mass balance, (vii) humidity and precipitation, (viii) evaporation, (ix) age and health of analyzed object during fixation of isotopes, (x) anthropogenic impact, (xi) postdepositional changes, (xii) other factors. The role of these factors will be discussed during presentation and some examples will be shown. Most of the audience most probably will conclude that most of the up to the date environmental models have to be revised (in the most).

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#### Cenospheres from fly ashes of Łaziska power plant

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Cenospheres constitute a side-effect of hard coal burning process in power generation plants, their contribution does not exceed 1% of ash content. They are grains of spherical shape, in most cases colourless or milky. Inside, they are filled with gases generated in the combustion process. Due to their characteristic composition, these tiny ash particles are particularly vulnerable to dusting. Spherical grains dry fast; captured by winds, they are transported to long distances, causing air and water pollution.

The scope of the paper is the discussion of the results of tests on cenospheres samples obtained from fly ashes of Łaziska Power Plant. The averaged cenospheres sample was subjected to chemical analysis, involving the determination of basic components and selected toxic elements. Also, basic physical properties important in view of industrial assessment and options of their disposal were determined.

The dominating constituents of cenopspheres are: silicon dioxide  $(SiO_2)$  and aluminum oxide  $(Al_2O_3)$ , the percentage of which is:  $SiO_2=54.9$  % and  $Al_2O_3=28.5$  %. Such high concentration of the above mentioned components is due to the aluminosilicate glassy phase and the presence of partly crystallized mullite, as substantiated by X-ray diffractometry. The total fraction of other elements, i.e.: Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, K<sub>2</sub>O does not exceed 16 %.

In view of glassy structure, similar to pearl stone low bulk density (below 0.5 kg/m<sup>3</sup>), good granular composition, with considerable percentage of the class below 0.25 mm, as well as high refractoriness (sP-147), the analysed cenospheres may be used as raw material for thermal insulation, offering an alternative for imported pearl stone. The release of gases ( $CO_2$  and  $N_2$ ), determined by means of thermal tests, indicates that the tested cenospheres may also serve as effective fire-protection materials. Moreover, due to high refractoriness, the tested cenospheres may be used as founding powder in steel casting, or for manufacturing light concrete with improved thermal-insulating properties, especially in consideration of easy extraction method and low costs involved.

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#### Weathering process of Morasko and Pułtusk meteorites

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Morasko and Pułtusk meteorites represent two different types of interplanetary matter. The Morasko meteorite is classified as an iron-type meteorite (IAB), whereas the Pułtusk one represents a stony meteorite, in particular ordinary chondrite H5 (brecciated). The source area for the Morasko meteorite is most probably the planetoide 4 Westa type, while the Pułtusk meteorite comes from the 6 Hebe planetoide. The Morasko meteorite was discovered in 1914, and its fall is estimated for 3 500 – 5 000 years ago. The Pułtusk meteorite fell down 140 years ago.

Petrographical investigations were carried out using both reflected and transmitted microscopy and mineral phases were identified both optically and using X-ray diffraction. Chemical composition of minerals was determined using a scanning electron microscope equipment of an EDS (EDAX) detector (Scanning Microscopy Laboratory, Faculty of Earth Sciences, University of Silesia, Sosnowiec) and a Cameca SX 100 electron microprobe (Inter-Institutional Laboratory of Microanalysis of Minerals and Synthetic Substances, Faculty of Geology, Warsaw University).

In both meteorites, only metallic phases: kamacite, taenite, tetrataenite and in a small extent troilite, underwent weathering. In case of the Morasko meteorite also schreibersite and cohenite show weathering. In both meteorites, in near-surface zones among the Fe<sup>3+</sup>-hydrooxides the secondary high-Ni metallic phases occur. They represent native nickel or awaruite Ni<sub>3</sub>Fe. Rarely non-stoichiometric Ni-sulphides with Fe admixtures formed. Only in small cavities in the Pułtusk meteorite was found millerite NiS. Awaruite or native nickel is usually found as thin coatings on small rhabdite crystals occurring in phosphates and chlorides. In mild climate conditions slow weathering of iron and stony meteorites occur. In the soil environment the presence of could cause reductive conditions in some places. During oxidation of metallic phases, a substantial Ni meteorite concentration took place in a form of metal and sulphide minerals. The main products of weathering – iron hydroxyoxides and partly carbonates – are enriched in Ni in relation to primary metallic phases. In secondary high-Ni metallic phases the strong enrichment in Ge (5.02% at) and partly in Ga (0.29% at.) occurs. That might be an evidence for a strong siderophile tendency of these elements in hypergene conditions.

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#### Experimental study of blast furnace slag hydrothermal transformation - preliminary study

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Blast furnace (BF) slag is a co-product of metallurgical processes of pig iron production. It can be used as a replacement material for cement or as a road construction material, what gives economic and environmental benefits (Escalante et al., 2001). BF slag is composed of reactive mineral phases which may contain harmful elements. Usually, concentration of toxic elements like Se, Cr, Pb, Cd, As, and so on, are not very high, and these elements are strongly bounded within slag components (Proctor et al., 2000). However, BF slag may contain also other elements like sulphur.

The aim of this study is to simulate long-term processes of slag decomposition in presence of solutions of different composition and different pH value, which are responsible for slag dissolution and release of harmful slag components.

Experiment was taken in Soxhlet apparatus, under hydrothermal conditions (in temperature of boiling solution). Extracted material and after-reaction solution were analyzed using XRD and SEM-EDS.

First experiment was made to check reactivity of investigated slag in distilled water (pH value ~ 5.8). Two types of BF slag were analyzed: "fresh slag" - sample 628 (from year 2006), and "old" slag - sample 629 (from 80's XX century). The output samples consist of mineral phases typical for this type of slag. In sample 628 akermanite, gehlenite, rankinite and orthoclase occurred, and in sample 629 akermanite, gehlenite, calcium silicate oxide (no of PDF card 02-0506), and tremolite were determined.

Each sample of slag was treated in hydrothermal conditions for 24h and 120h. After 24 h experiment in sample 628 only slightly changes in slag composition were noted. The main mineral phases are akermanite, gehlenite, calcium silicate oxide (wollastonite). In sample 629 the main phases are gehlenite, calcium silicate oxide (wollastonite) and melilite (probably instead of tremolite

After evaporation of after-reaction water solution in sample 628 we can observe crystallization of gypsum, hannebachite, sulphur and calcite. In evaporated solution, of sample 629, only gypsum crystallized.

After 120 h experiment phase composition changed significantly. In sample 628 melilite, rankinite and calcium silicate oxide (wollastonite) are present as dominant phases. From after-reaction solution gypsum, calcite, and akermanite crystallized. In sample 629 beside typical components like akermanite, gehlenite also larnite and hydrated calcium silicate oxide – xonotlite crystallized. In evaporated solution only gypsum crystallized.

Experimental study indicates that analyzed BF slag is reactive in distilled water under hydrothermal conditions. Results of this study indicates that formation of new phases is

quite limited and leaching is restricted to S, Ca. Leaching of S can cause harmful influence on environment but also can cause accelerated damage of concrete construction.

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# Experimental study of steel production slag hydrothermal transformation – preliminary study

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The studied slag is a co-product of metallurgical processes, formed in steel production. It is used as a raw material in road and concrete constructions, but also in others fields of industry (Yan et al., 1999; Motz, Geiseler, 2001). Slag is composed of high-temperature phases, which can be reactive for many years and cause the release of harmful elements into environment. This is the reason why recently slags are investigated as a waste material that can cause environmental impact and also can be dangerous for human health.

The aim of this study is to simulate long-term processes of slag decomposition in changing conditions (different composition of solutions and different pH). The pH value is one of the most important parameter for dissolution of slag, and for release behavior of toxic elements (Yan et al., 1999).

Experiment was conducted under hydrothermal conditions (in temperature of boiling solution) in Soxhlet apparatus. Extracted material and after-reaction solution was analyzed using XRD and SEM-EDS.

First experiment was made to check reactivity of investigated slag in distillated water (pH value ~ 5.8). Two types of steel slag were analyzed: "fresh slag" - sample 626 (from year 2006), and "old" slag - sample 627 (reserves from year 2002). The output samples consist of mineral phases typical for this type of slag: calcium ferrites (srebrodolskite, brownmillerite), larnite , but also other Ca-Fe-Mg-Mn oxides and silicates.

Each sample of slag was treated in hydrothermal conditions for 24 h and 120 h. After 24 h experiment in both samples no changes in phase composition were noted (main phases are calcium ferrite and larnite). After evaporation of after-reaction water solution we can observe crystallization of calcite. It indicates that Ca dominate as an element leached form the slag After 120 h experiment phase composition changed slightly. In sample 626 main phases are calcium ferrite, larnite and wüstite. From after-reaction solution only calcite crystallized. In sample 627 beside typical components like calcium ferrite and larnite also bicchulit (watered ghelenite) is present. In evaporated solution calcite and aragonite crystallized.

Experimental study indicates that analyzed steel slag is not very reactive in distilled water under hydrothermal conditions. Formation of new phases is very limited and leaching is restricted only to Ca.

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# Gold mineralization and geochemical exploration in Loean area, central Iran

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Loean area is located NW of Saveh city in markazi province. Based on structural division of Iran, studied area is part of the Oromieh-Dokhtar magmatic belt. The area includes Eocene volcanic series (trachyandesitic to andesitic lava), Oligo-Miocene sediments (Qom formation: limestone and marl) and intrusive rocks. The intrusive rocks which are host of the gold mineralization range in composition from monzonite to diorite and quartz-monzonite. Geochemically, the intrusion shows calk-alkaline trend. Tectonic diagrams show that the intrusion is related to intra-plate continental basalt.

The results of optical microscopy show that major minerals of intrusive rocks are Plagioclase, Amphibole, and Pyroxene, while minor minerals include Epidote, Calcite, and Olivine. The most common alterations in the Loean area are serecitizatione and kaolinitization. Gold mineralization developes in carbonate, pyrite, chalcopyrite, malachite, and covellite veins that are the most important veins in the mineralization zone. Mineralization correlates with the strike of a regional fault (S75-80E). 918 samples were collected and analyzed with ICP and fire assay (for Au) methods for geochemical exploration. The results of geo-statistics interpretation of the results show anomalous concentration of gold in quartz. Gold occurs also as epithermal veins. The highest gold content in mineralized zone is 999 ppb in the faulting zone with W-E trend.

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## Pyrometallurgical slags – analogs of natural geological materials and potential hazard for the environment

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Pyrometallurgical slags derived from smelting of various types of metallic ores, either sulfide or silicate, comprise similar phase assemblages. Phase composition however, which reflects the bulk chemistry, may vary significantly between various reworked ores. Smelting slags formed at high temperatures (over 1000°C) and consist mostly of silicate glass, synthetic equivalents of clinopyroxene, melilite, olivine and spinel. Many slags contain also various sulfides and/or intermetallic compounds which may often concentrate some metallic elements potentially hazardous to the environment.

Generally, chemical and phase composition as well as textures of slags are similar to some geological materials such as volcanic rocks. Moreover, slags exposed to atmospheric conditions undergo the same weathering processes as rocks.

Main components of slags such as silicates and oxides are known to be resistant to weathering. However, a potential environmental hazard may be related to small inclusions of sulfides and/or metallic compounds which are generally considered as more reactive than silicates and oxides. Since these inclusions are trapped within stable silicates or silicate glasses their reactivity is limited. However, if they are sufficiently abundant to constitute an interconnected network, the preferential weathering of sulfides and/or metallic compounds along the network may increase the rate of weathering of the surrounding phases. Also, weathering of vitreous slags resulting from smelting of Ni ores is enhanced by the agricultural practices.

An immediate risk of release of some potentially hazardous elements to the environment depends on the breakdown of main slag constituents (glass and silicates) and proportions of potentially reactive sulfides and/or metallic compounds. Furthermore, local conditions (climatic conditions, soil pH etc.), in the areas of slags storage, should be examined in order to predict the environmental impact of that industrial waste.

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## Synthesis of mimetite-vanadinite, and pyromorphite-vanadinite solid solution series

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Mimetite  $Pb_5(AsO_4)_3Cl$ , vanadinite  $Pb_5(VO_4)_3Cl$ , and pyromorphite  $Pb_5(PO_4)_3Cl$  are minerals isostructural with apatites. Due to anionic substitutions natural pyromorphite usually contains admixture of arsenates or vanadates and mimetite or vanadinite contain admixture of phosphates. The structural and thermodynamic properties of minerals from pyromorphite-mimetite series are well known. They can be easily synthesised in the laboratory, and the solid solutions series of these minerals is continuous. However, the knowledge on properties of vanadinite and its solid solutions is sparse. This is partly due to the lack of an effective method of synthesis of these minerals.

In order to investigate the mechanisms of anionic substitutions in lead apatites, an effective method of synthesis of vanadinite and its solid solutions has been proposed. Pyromorphite, mimetite, vanadinite and their solid solutions from vanadinite-pyromorphite and vanadinite-mimetite series have been synthesized from aqueous solutions by dropwise mixing of Pb(NO<sub>3</sub>)<sub>2</sub>, NaVO<sub>3</sub>, KH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>HAsO<sub>4</sub> and KC1 at 100°C and pH=3. X-ray Powder Diffraction (XRD), scanning electron microscopy (SEM/EDS), and infrared spectroscopy (FTIR) were applied to identify and characterize the precipitates. Both vanadinite-pyromorphite and vanadinite-mimetite solid solutions series appeared to be continuous. Application of XRD and FTIR analysis for semi-quantitative determination of anionic substitutions in lead apatites is proposed.

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#### Mimetite formation from lead adsorbed on surface of Bacillus Subtilis

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Bioavailability of arsenic in contaminated soils and wastes can be reduced to insignificant levels by precipitation of mimetite  $Pb_5(AsO_4)_3Cl$ . This results in conversion of bioavailable arsenate ions into a highly immobile mineral form resulting in neutralization of the toxicity without removal of toxic species from soil. Research regarding the reactions between  $AsO_4^{3^-}$  ions in the solution and soil particles does not explain all the mechanisms of reactions taking place in environment. The least is known on the role of microorganisms in the system. *Bacillus subtilis* is a well characterized Gram-positive aerobic bacteria commonly found in ground water and soil systems. The cell walls of Gram-positive species are highly porous. The adsorption of the lead ion onto surfaces of non-metabolizing bacteria is partly reversible. The adsorption of lead onto *Bacillus subtilis* are controlled by pH (effectiveness of adsorption increase with increasing pH) and ionic strength.

The objective of this study was to explicate the mechanisms of the reaction between solution containing lead ions and arsenates adsorbed on non-metabolizing bacteria *Bacillus subtilis* surface saturated with adsorbed  $Pb^{2+}$ . The reaction, in the presence of CI results in rapid crystallization of mimetite crystals on the surface of bacteria cells (heterogeneous precipitation) as well as in the space between them (homogeneous precipitation). The mechanism of nucleation and precipitation. Heterogeneous precipitation and formation of mimetite incrustations on bacterial cells indicate that desorption of lead from Gram-positive bacteria is slower than precipitation of mimetite. At the conditions of our experiment, homogeneous crystallization of pyromorphite is a result of reaction between ions in intergranular solution.

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## Sulfides oxidation in mine tailings material from the antimony deposit Dúbrava (Nízke Tatry Mts.)

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In the second half of  $20^{\text{th}}$  century Dúbrava Sb deposit was the main antimony producer not only in former Czechoslovakia, but also in Central Europe. The effect of mining on the surrounding environment was very intensive. Contamination of this region is very high. One of the contamination sources are four tailing impoundments. The major type of contamination is toxification (Sb, As), acidification is insignificant (pH 7 – 8). Stibnite is very unstable in oxidation conditions, dissolves quickly and spreads into surrounding environment (Ashley et al., 2003).

The main effect of oxidation can be easily seen in the samples of tailing material taken near the tailings surface. Different levels of oxidation and various products of sulfides oxidation were observed. Pyrite is the most abundant sulfide mineral. Additionally, the tailings frequently contain arsenopyrite and less frequently stibnite. Pyrite as well as arsenopyrite grains are altered by oxidation in the form of oxidation rims. The rims on pyrite are mostly composed of Fe - oxihydroxides containing up to 45 at.% of Fe, up to 2 at.% of As and up to 1.2 at.% of Sb. The rims developed on arsenopyrite grains contain up to 37 at.% of Fe, up to 12.5 at.% of As and up to 2.5 at.% of Sb. Content of As and Sb in the rims increases in the direction away from sulfides cores in both cases. Secondary rims are mostly destructed and are subsequently extracted from the sulfide core. We have not observed the presence of secondary oxides connected with stibnite grains. Based on the presence of fractures in stibnite and significant evidence for Sb presence in pore waters we suggest that Sb is leached from stibnite into the solutions; later, aqueous Sb is sorbed by secondary Fe oxyhydroxides present in the system.

Various Fe and Sb-Fe oxides and oxihydroxides are also common in tailing material. Some of them are directly connected with sulfide minerals, such as goethite pseudomorphs after pyrite. In other cases the origin is uncertain. Fe-oxihydroxides containing up to 42 at.% of Fe bind a large amount of Sb (up to 2 at.%) and only a small amount of As (up to 0.2 at.%). Sb–Fe oxihydroxides contain up to 23 at.% of Fe, up to 19 at.% of Sb, and up to 0.7 at.% of As.

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## Iron arsenates from Dlouhá Ves near Havlíčkův Brod deposit, Czech Republic

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The deposit Dlouhá Ves near Havlíčkův Brod is situated in the variegated unit of the Moldanubian zone, hosted by biotite-sillimanite gneisses and migmatites. The deposit was mined until 1966 for polymetalic sulphide minerals. Major part of the vein material consists of quartz and carbonate. Primary ore minerals are pyrite, arsenopyrite, pyrrhotite, chalcopyrite, sphalerite and galena. Alteration and weathering of the ore minerals produced supergene (sub)recent assemblages with prevailing amorphous hydrous ferric oxides, jarosite, gypsum and scorodite and uncommon covellite, chalcocite, bornite, chrysocolla, malachite, melanterite and rare pharmacosiderite and kaňkite.

Since the end of mining operations at 1966, the weathering processes extensively decomposed the ore minerals on waste dumps, producing hydrous iron oxides, sulphates, carbonates and arsenates. Under mostly oxidizing conditions, decomposition of arsenopyrite took place, yielding scorodite, kaňkite, pitticite and iron hydroxides as the weathering products. Scorodite is a typical mineral of upper parts of the dumps; the mineral was identified by X-ray powder diffraction. Scorodite forms thin, yellow or green coatings and incrustations on arsenopyrite surface and fragments of ore material. The occurrence of kaňkite in Dlouhá Ves is the first in the mining district of Havlíčkův Brod. Kaňkite occurs on weathered arsenopyrite, together with scorodite, pitticite and amorphous iron oxides. The mineral was identified by X-ray powder diffraction, refined unit-cell parameters of kaňkite [a=18,83(2) Å, b=17,45(2) Å, c=7,601(4) Å] correspond to the published values. Chemical composition data suggest slight substitution of S for As. Chemical study of both As-minerals proved their inhomogeneous chemical composition, occurrence of AsS<sub>-1</sub> substitution and variable H<sub>2</sub>O content. Amorphous hydrous ferric oxides contain increased content of arsenic (up to 2.2  $As_2O_5$ ). At the surface of amorphous hydrous ferric oxides, a younger minerals, for example gypsum and rozenite, form during dry periods.

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## Mineralogy and alteration pattern of the Biely Vrch Au-porphyry deposit, Slovakia

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Biely Vrch deposit is a new economic Au-porphyry mineralisation in Slovakia discovered by the EMED Mining, Ltd. The deposit is located in the central zone of the Neogene Javorie stratovolcano, and shares many properties with Au-porphyry deposits, especially those in the Maricunga Belt in N Chile, including the lowest Cu/Au within porphyry types deposits (<0.04 %Cu/ppm Au at B. Vrch).

Parental intrusion of diorite to andesite porphyry and its andesitic volcanic host rocks are affected by extensive alteration, dominated by intermediate argillic (IA) alteration represented by I-S, illite, chlorite, pyrite  $\pm$  apatite, rutile, epidote. It variably overprints earlier high-T K-silicate (K-feldspar, biotite, magnetite/ pyrhotite) and Ca-Na silicate (intermediate to basic plagioclase, actinolite) alteration in deeper levels of the system, respectively. Propylitic/chloritic alteration (smectite, CS/corrensite, chlorite, quartz, pyrite) represents outer zone of the system. Ledges of advanced argillic (AA) alteration (pyrophyllite, dickite, kaolinite, vuggy quartz  $\pm$  pyrite, alunite, dumortierite) correspond to the youngest stage of alteration.

Several generations of veinlets are present. The oldest A-type veinlets (biotitemagnetite-quartz  $\pm$  K-feldspar, spinel, sericite?) are associated with K-silicate alteration. Younger quartz veinlets are the most common type. At least 3 generations have been recognized, some of them showing banded texture, resulting from high content of vaporrich fluid inclusions and micrometer-sized magnetite  $\pm$  chalcopyrite, pyrite grains. Botryoidal textures are continuous across quartz grains, suggesting recrystallization from silica gel. Central part of some veinlets is filled up by pyrite, chalcopyrite  $\pm$  magnetite, marcasite, galena, sphalerite. They also occur as individual veinlets affiliated to IA alteration. Clay veinlets (illite, I-S, chlorite  $\pm$  epidote, apatite, rutile, pyrite, magnetite, pyrophyllite veinlets ( $\pm$  dickite, pyrite, rutile) occur only in places affected by AA alteration. Carbonate-zeolite veinlets ( $\pm$  epidote, marcasite) are younger than IA veinlets, but are thought to be older or coeval with AA alteration. Rare, solitary molybdenite occurs within late fissures.

Gold grains usually occur in the vicinity of quartz veinlets, in altered rock with clays (illite, I-S), chlorite and K-feldspar. Gold measures usually 2-15, rarely up to 40  $\mu$ m, and contains 3-7 wt% of Ag, and traces of Hg and Cu. Crystallization of quartz from silica gel

was probably induced by fluid decompression due to shallow level of emplacement and/or to dynamic paleosurface degradation, resulting in destabilization of Au-complexes.

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# Isotopic signature of the Siberian flood basalts and alkaline magmatism of Polar Siberia

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A close association between alkaline magmatism and continental flood basalts is observed worldwide. Nevertheless, the problem of a genetic link between the Siberian flood basalts (SFB) and the ultramafic-alkaline rocks of the Maimecha-Kotuy province in Polar Siberia is still being debated. The SFB with a volume of  $1.6 \times 10^6$  km<sup>3</sup> occur in the northern part of the Siberian platform. The Putorana plateau, where about 90% of all the basaltic volcanism occurred, is located in the centre of the SFB province. The ultramafic-alkaline Maimecha-Kotuy province occupies about 74,300 km<sup>2</sup> and is located to the Northeast of the SFB. It comprises the world's largest ultramafic-alkaline Guli massif, the ultramafic-alkaline-phoscorite Kugda complex, and 31 smaller ultramafic-alkaline intrusions.

A whole-rock U-Pb age of 250±9 Ma was determined for the Guli massif, which lies within the range of ages previously reported for the SFB. The combined Pb, Sr, and Nd isotopic systematics of the SFB and the Guli and Kugda alkaline rocks identify several discrete source components. The first component dominates many of the Guli rocks and is characterized by low 87Sr/86Sr (0.7031 to 0.7038), high (Nd (+5.35 to +3.97), and relatively non-radiogenic Pb (206Pb/204Pb = 17.88-18.31; 207Pb/204Pb = 15.38-15.46; 208Pb/204Pb = 37.33-37.70), which we associate with the depleted (or MORB source) upper mantle. The second component dominating the Putorana basalts and many of the other SFB demonstrates a notable chemical and isotopic uniformity with 87Sr/86Sr values of 0.7046 to 0.7052,  $\varepsilon_{Nd}$  values of 0 to +2.5, and an average Pb isotopic composition of 206Pb/204Pb = 18.3, 207; Pb/204Pb = 15.5; 208Pb/204Pb = 38.0). This component is speculated to derive from a relatively primitive, lower mantle plume with a near-chondritic isotopic signature. The third mantle component characterizing most of the Kugda massif and some dykes is not as depleted as the Guli source, but more depleted in respect to the Rb-Sr system than the Putorana basalts.Contamination by upper and lower continental crustal material, designated as components 4 and 5, is postulated to explain the isotopic characteristics of some of the higher SiO<sub>2</sub> rocks of the Guli and Kugda massifs and the SFB. Finally, metasomatic processes associated with the invasion of the Siberian superplume add a sixth component responsible for the extreme enrichment in rare-earth and related elements found in some Guli and Kugda rocks and in the SFB.

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# The influence of mineralogical and petrological composition on the trace element content in the rocks associated with the 308 coal seam (USCB)

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Concentration of trace elements (Ba, Cd, Co, Cr, Cu, Ni, Pb, Zn, Mn, Sr, Ge, Be, Li, V, As, Ga) in rocks overlying, intercalating and underlying the 308 coal seam were investigated. The samples were collected in vertical two profiles.

The above mentioned rocks are represented by sandstone (with clay-siderite-carbonate cement), claystones (kaolinite-illite) and sideritic claystone (kaolinite-chlorite-siderite).

The high content of Ba, V, Zn, Mn, Pb and Cu was observed in all samples, regardless of the petrographic composition of rocks. The content of these elements varies from tens to above 100ppm. Cr, Ni, Ga, Ge, Be and As contents are lower, and vary between a few to over ten ppm. The concentration of Co, Cd, Sr, Li varies from one to a few ppm.

The highest concentration of trace elements was found in argilites, where Ba, Pb, Zn, Ge and Li dominate. The highest content of Mn, Cu, Sr, Co, Cd was found in sideritic claystone sample. It suggests , that these elements are connected with carbonate minerals. In sandstone V, Cr, Ni, Ga, Ge are main trace elements. But There the correlation between amount of organic matter and the content of the trace elements was not observed.

Cr, Ni, Ge, Be, Li, V and Ga are enriched in rocks overlying the 308 coal seam, but are very low in the underlying rocks.

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#### Very low-grade metamorphism in the Variscan accretionary prism of the Kaczawa Complex (Sudetes, SW Poland): new data from illite "crystallinity" index

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Mélanges of the Kaczawa Complex (Sudetes, SW Poland) are widely understood to have been gravitationally redeposited within an oceanic trench. They were subsequently subjected to deformation and metamorphism during further evolution of the Variscan accretionary prism. The metamorphic conditions associated with this process are not well understood. In order to quantify the temperature conditions of the metamorphism, the illite "crystallinity" index was determined for mélange, turbidite, and various fine grained metasediments.

Samples used in this investigation were collected from the northern part of the Kaczawa Complex. Sites included exposures along the Kamiennik stream between Rzeszówek and Jurczyce villages (Rzeszówek-Jakuszowa Unit, RJU), and deep boreholes near Stanisławów (Chełmiec Unit, CU).

In order to determine the chemical composition of the white mica, 26 samples from both natural outcrops (RJU) and drill cores (CU) were analyzed with an electron microprobe (EMPA, 179 analyses in total). Authigenic grains commonly formed the matrix of the rocks and were less than 20 $\mu$ m in size. Elsewhere, they occurred as intergrowths with chlorite (chlorite-mica stacks), usually less then 100 $\mu$ m in size. All the grains analysed were K-micas containing minor amounts of paragonite (Na/(Ca+Na+K) less than 0.33) and margarite (Ca/(Ca+Na+K) 0.00-0.02). Fe<sub>tot</sub>, Mg and Mn content (Fe<sub>tot</sub> + Mg + Mn ) ranged from 0.18 to 1.31. The white micas from the turbidite series of RJU are chemically more similar to muscovite, while phengite-like compositon is characteristic for metamudstones from CU.

The metamorphic conditions were established on the basis of the illite "crystallinity" index (IC) determined by X-ray diffraction (41 samples analysed in total). The average IC value for RJU samples is 0.37 while CU samples have an average value of 0.33. The dark-coloured metamudstones from CU (including the mélange) and the mélanges of Rzeszówek (RJU) have undergone very low-grade metamorphism (anchizone), at temperatures of 200-300°C. Temperatures for parts of the turbidite sequence in the Kamiennik stream (CU) may have been even lower, and sediments are likely to have undergone late diagenesis (150-200°C).

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#### Two types of ultrapotassic magmatic rocks in the Bohemian Massif – coeval intrusions at different crustal levels

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Ultrapotassic plutonic rocks form numerous bodies in the internal (Moldanubian) Zone of the Bohemian Massif. They feature specific geochemical composition and mineral zoning, indicative of the complex genesis and evolution of the magma. U-Pb zircon dating of these rocks commonly yields discordant ages, the interpretation of which is equivocal.

Two-pyroxene-biotite melasyenite of the Jihlava Pluton, representing a less abundant group of the ultrapotassic plutonic rocks, shows a less complex magmatic evolution, and therefore it was selected for our study. The rock preserves a dry primary mineral assemblage orthopyroxene-clinopyroxene-K-feldspar-plagioclase±quartz, and signs of high-temperature crystallization (rutile needles in K-feldspar and orthopyroxene, exsolution lamellae of Cpx in Opx). It contains predominantly equant, rounded multi-facetted and tabular zircon grains with well-developed crystal faces, showing sector and oscillatory zoning in CL. Three microfractions and one single zircon analysis perfectly agree with each other and yield a precise concordia age of  $335.2 \pm 0.54$  Ma (MSWD = 0.28). This age is interpreted as dating high-temperature magma crystallization in the lower crust.

A typical representative of the ultrapotassic rock series from the Třebíč Pluton, pophyritic amphibole-biotite melagranite, consists of K-feldspar, plagioclase, quartz, and abundant biotite and amphibole. Zircons are of two types: short to long prismatic crystals and tabular grains. Crystal faces are usually well-defined and sharp. Zircons of both types show oscillatory zoning and some inherited cores. Five analysed prismatic and tabular zircon microfractions and single grains are aligned along a discordia intersecting the concordia at  $334.8 \pm 3.2$  Ma (MSWD=0.14). Only one prismatic grain fraction shows inheritance and an older age of 338.1 Ma.

One zircon yielded a strongly discordant point with an upper intercept age of 2.2 Ga, which represents an old inherited crustal component (inherited cores in CL).

Our data show that the two rock types of the ultrapotassic (durbachite) series have identical age, which is consistent with one magmatic event forming potassic intrusions in different areas in the Bohemian Massif. We suggest that the different character of the rocks reflects different composition of the magmatic fluids (low vs. high  $aH_2O$ ) and different degree of fluid saturation. This can be explained by different depth of magma emplacement (lower vs. upper crust), relatively high exhumation rate of the Jihlava Pluton, or much more important interaction of magma with country rocks in the case of the Třebíč Pluton.

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# Apatite-ellestadite solid solution and associated minerals of metacarbonate slags from burning coal dump in Rydułtowy (Upper Silesia)

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Burning of coal-mining dumps causes thermal decomposition of the waste rocks. Three products of rock melting , namely paralavas (cordierite-rich nodules), metaargilites (hematite-rich clinker-like annealed shales) and metacarbonate slags, all mentioned i.e. by SOKOL et al. (2002), were found on a burning dump in Rydułtowy (Upper Silesia). They occur cemented together as blocks of pyrometamophic breccias. Sulfate silicate apatite-(CaF) (rock 1) and phosphate ellestadite-(CaF) Ca<sub>5</sub>(SiO<sub>4</sub>,SO<sub>4</sub>,PO<sub>4</sub>)<sub>3</sub>F (rock 2), closely associated with Ca ferrites (srebrodolskite Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> and less common CaFe<sub>2</sub>O<sub>4</sub> phase), and spinel group mineral (Mn- and Al-bearing magnesioferrite) were confirmed by XRD, SEM-EDS and EPMA methods. The samples contain also quartz, aragonite, calcite, silicate glass, anorthite (sometimes barian) and a K-Pb(Ba) silicate phase. Srebrodolskite (a=5.56, b=14.77, c=5.43) and magnesioferrite (a=8.37) cell parameters), are very close to standards (PDF 01-071-2108 and 00-012-0261, respectively). XRD data for apatite-(CaF) of rock 1 is consistent with chemical data. Increase of its cell parameters (c=6.88, a= 9.42) when "moving" to less phosphatian ellestadite-(CaF) (PDF 00-045-0009) are explained by an increase of "a" with decrease in phosphorus content (ROUSE & DUNN, 1982). Similar pattern is observed in F substituted apatites. Final decomposition products include lime (and/or portlandite), (ferro)periclase and hematite. Reaction between hematite and periclase (at 850-1100°C) gives magnesioferrite (SOKOL et al. 2002), while Ca ferrites can be produced by hematite-lime or magnesioferrite-calcite interactions (FILIPPIDIS et al. 1996).

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#### The first geochronological and isotopic-geochemistry data of the detrital zircons from Ediacaran sandstones of Engane-Pe uplift (Western Polar Urals): comparison of peri-gondwanan terrains and pre-uralides - timanides

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The Pre-Uralides-Timanides are Neoproterozoic complexes, located in the east and northeast frame of Baltica (Kuznetsov et al., 2007). Pre-Uralides-Timanides are believed to be a relict of the Western continuation of the Late-Neoproterozoic Cadomian-Avalonian (Peri-Gondwanian) subduction belt, which was formed along a margin of the Gondwana (Linnemann et., 2007), or a relict of the Late-Neoproterozoic Cadomian or gen, which was formed as a result of collision of Timanian-Uralian margin of Baltica and Peri-Gondwana (Puchkov, 1997).

The U-Pb isotopic ages and features of the Lu-Hf isotopic system of the 47 grains of detrital zircons (ZR) from Ediacaran sandstones of the Engane-Pe Fm. (Engane-Pe uplift, Western Polar Urals) were obtained at GEMOC Center, Australia (Natapov L.M., Belousova E.A.). The one ZR-grain showed the Mezo-Proterozoic age (1143±20Ma). All others ZR-grains subdivided into two populations "A" and "B" (~65% and ~35% ZR, respectively). The "A"-ZR are represented by grains of weekly-rounded morphology and corroded fragments with ages ranging between 760-675 Ma. The "B"-ZR are represented by euhedral prismatic crystals or fragments of such crystals with ages ranging from 670 to 590 Ma. The model ages  $T_{DM}^{C}$  (approximation of the minimum age for the source material of the magma from which the ZR crystallized) of "A"-ZR range from ~0.84 to ~1.76 Ga, and of "B"-ZR is ~1.28 Ga, and of ZR<sub>(-1143 Ma)</sub> is ~1.76 Ga.

The  $T_{DM}$  of magmatic rocks and U-Pb ages of detrital ZR of Neoproterozoic complexes of Peri-Gondwanan terrains (Linnemann et., 2007; Murphy et al., 2006) differ essentially from the obtained  $T_{DM}^{\ \ C}$  and U-Pb ages of detrital ZR of Pre-Uralides-Timanides.

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#### Crystal structure and physical properties of a new platinum-group mineral Pašavaite, Pd<sub>3</sub>Pb<sub>2</sub>Te<sub>2</sub>

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Pašavaite,  $Pd_3Pb_2Te_2$ , is a new palladium mineral species discovered at the Talnakh deposit, Taimyr Autonomous District, Russia. It was observed in two polished sections, where it occurs as subhedral grains not exceeding 20 µm in diameter embedded into polarite, and randomly accompanied by unknown Pd-Pb-Bi-Te phases and sperylite or intergrown with Au-Ag phases. The mineral is named in honour of Dr. Jan Pašava, for his role in long-term investigations of geochemistry of Platinum Group Elements, and his significant contribution to research on PGE deposits. The mineral and the mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification of the IMA (CNMNC 2007-059).

Pašavaite could not be isolated for a thorough characterization due to its very small grain-size. Therefore, the analogue was synthesised. This synthetic  $Pd_3Pb_2Te_2$  phase was used to determine physical properties, to measure reflectance, to collect powder data and to resolve the crystal structure. The stoichiometric amounts of respective elements were loaded into silica glass tube and heated in furnace at 400°C for 5 months.

Pašavaite is orthorhombic, space group *Pmmn*, *a* 8.599(1), *b* 5.9381(6), *c* 6.3173(8) Å, V 322.6(1) Å<sup>3</sup> and Z = 2. Its crystal structure can be described as a layered structure formed by face-shared [PdPb<sub>4</sub>Te<sub>2</sub>] octahedra running parallel to (001). Two independent palladium atoms are surrounded by four lead and two tellurium atoms showing distorted octahedral coordination with tellurium atoms in *trans* positions with respect to one another. Two independent lead atoms are coordinated by six palladium atom in two different ways. The crystal structure of pašavaite shows many structural similarities to the structure of shandite (Ni<sub>3</sub>Pb<sub>2</sub>S<sub>2</sub>,  $R \overline{3} m$ ) and parkerite (Ni<sub>3</sub>Bi<sub>2</sub>S<sub>2</sub>, C2/m).

The structural identity of pašavaite and synthetic material was confirmed by results of the electron back-scattered diffraction (EBSD) study. The EBSD patterns (also known as a Kikuchi bands) obtained from natural grains easily matched the patterns generated from structure data of  $Pd_3Pb_2Te_2$  provided by our crystal structure solution.

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#### Two contrasting fluids controlling strong mobility of U, Zr and REE, and their implication to the origin of the Rožná U-deposit (Moldanubian Zone, Bohemian Massif)

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The Rožná-Olší uranium ore field is located in the northeastern part of the Moldanubian Zone of the Bohemian Massif. K-Ar ages of illite from synore alteration yielded  $277.2 \pm 5.5$  to  $264.0 \pm 4.3$  Ma. (Kříbek et al. 2008)

Three major textural types of uranium mineralization were recognized at the Rožná deposit (1) **Vein mineralization** with uraninite > coffinite ( $\pm$ montroseite) in carbonate veins (2) **Episyenite mineralization** with disseminated coffinite, U-Zr silicates, U-bearing hydrozircon and complex U-Zr-Ti -Si phases in desilicified, albitized and hematitized rocks, and (3) **Zone mineralization** with disseminated coffinite > uraninite > U-Zr-silicates, and complex U-Zr-Ti -Si phases developed in chloritized, pyritized, carbonatized and graphite-enriched cataclasites.

Episyenitization affects mainly paragneisses and migmatites, whereas amphibolites, pegmatites or granites are less affected. Episyenites are macroscopically apparent by their distinct rose to red color. In thin sections and BSE images primary plagioclase is replaced by albite, white mica and hematite, biotite or amphibole by chlorite, and quartz is leached out. The uranium ore minerals in episyenite mineralization commonly replaced primary minerals with  $Fe^{2+}$  - biotite, pyrite and pyrrhotite. This feature indicates the presence of oxidizing fluids transporting  $U^{6+}$  ions, which were reduce at the contact with minerals containing Fe<sup>2+</sup> ions. On the contrary common collomorphic textures of uraninite and euhedral shape of coffinite crystals indicates precipitation in the open space. No replacement of older minerals by late U-bearing phases was observed. The ore minerals from the vein mineralization are rich in vanadium and lead, whereas uranium ores from episyenite are depleted in these elements, but the elevated concentrations of Zr, La, Ce,Y, Ti and F are typical. The episyenite mineralization and vein mineralization (carbonate veins) at the Rožná deposit represent two distinct and easily recognizable types of ore mineralization, distinct in textures, mineral assemblages and mineral chemistry. Two different types of fluids were probably responsible for the origin of these two mineralizations. In contrast the zone of mineralization is highly variable and it can be hardly characterized in simple and unambiguous way.

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# Clay minerals in different horizons of cambic soil made from phonolite of Opolno-Zdroj area, Sudety Mts., SW Poland

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Phonolites are an igneous volcanic rocks with low silica content, indicating intermediate composition between felsic and mafic. Build up of feldspathoids (mainly nepheline) and alkali feldspar (mainly sanidine). Phonolites are silica under-saturated, and rich in alkalis and aluminium. Accessory phases include titanite, apatite, corundum. zircon, magnetite and ilmenite. Because the under-saturated lavas eruptions are very rare those rocks are known only from Canary Islands, Scotland, Brazil, Sardinia, British East Africa, New Zeland, and small occurrences in Cornwall, Bohemia, Auvergne. There are very few data connected with the weathering processes of phonolites, especially knowledge on clay minerals derived in temperate climate is very small. The aim of this paper was to determine clay minerals developed during weathering processes of phonolite located in Opolno-Zdroj area, Sudety Mts, SW Poland. X-ray diffractograms of clay fraction separated from different horizons of cambic soil developed from phonolites will be presented and discussed at the poster.

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#### Chemical composition of columbite-group minerals from selected pegmatites in the Góry Sowie Mts, Strzelin-Žulova AND Hruby Jesenik Massifs – preliminary data

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The paper presents results of electron microprobe studies of columbite-group minerals from pegmatites in the Sudety Mts of different origin. Samples have been collected from metamorphosed pegmatites in the Owiesno-Kietlice area (Góry Sowie gneissic block), magmatic, hydrothermally altered pegmatites in the Strzelin quarry (the Strzelin-Žulova granitoid massif) and from highly fractionated, metamorphosed pegmatites in Branna, Velke Losiny and Petrov upon Desna (the Hruby Jesenik metamorphosed massif). Chemical analyses of samples were made using a CAMECA SX-100 microprobe in the Inter-Institution Laboratory for Microanalysis of Minerals and Synthetic Substances at the Faculty of Geology, Warsaw University.

Minerals of the columbite-group in Góry Sowie Mts were found in metamorphosed pegmatites, which mainly consist of plagioclase, quartz, muscovite, accessory tourmaline, beryl and kyanite. Idiomorphic crystals of Nb-Ta oxides reach up to 100  $\mu$ m in size. Ferrocolumbite from Kietlice shows low Ta/(Ta+Nb) ratio varying between 0.007-0.131, and almost constant Mn/(Mn+Fe) ratio varying in the range from 0.351 to 0.410.

(Nb,Ta)-bearing pegmatites in the Strzelin-Žulova massif form veins intersecting host granitoids. The veins are composed of plagioclase, K-feldspar, quartz, muscovite, accessory chlorite, beryl and pyrite. Columbite forms idiomorphic crystals up to 50  $\mu$ m in length. The approximate ferrocolumbite formula from the Strzelin quarry is: (Fe<sub>0.65-0.68</sub>Mn<sub>0.29-0.30</sub>Mg<sub>0.00-0.01</sub>)(Nb<sub>1.66-1.85</sub>Ta<sub>0.14-0.33</sub>Ti<sub>0.01-0.02</sub>W<sub>0.01-0.02</sub>)<sub>2</sub>O<sub>6</sub>. Similarly, both Ta/(Ta+Nb) ratio as well as the Mn/(Mn+Fe) ratio varying in very narrow ranges from 0.069 to 0.164 and from 0.299 to 0.314, respectively.

Minerals of the columbite group in the Hruby Jesenik massif occur in pegmatites composed mostly of plagioclase, albite, quartz, biotite, chlorites, ilmenite and pyrite. The (Nb,Ta)-oxides form idiomorphic crystals up to few millimeters with distinct variation in chemical composition from the core to the rim. They represent ferrocolumbite ( $Fe_{0.50-0.75}$   $Mn_{0.10-0.37}Mg_{0.05-0.10}$ )(Nb<sub>1.09-1.61</sub>Ta<sub>0.32-0.83</sub>Ti<sub>0.07-0.15</sub>W<sub>0.00-0.01</sub>)<sub>2</sub>O<sub>6</sub>, ferrotantalite ( $Fe_{0.63-0.71}Mn_{0.18-0.34}Mg_{0.02-0.11}$ )(Ta<sub>1.11-1.35</sub>Nb<sub>0.60-0.83</sub>Ti<sub>0.03-0.05</sub>W<sub>0.01-0.02</sub>)<sub>2</sub>O<sub>6</sub> and manganocolumbite ( $Mn_{0.65-0.71}$  Fe<sub>0.26-0.31</sub>Mg<sub>0.00-0.01</sub>)(Nb<sub>1.29-1.55</sub>Ta<sub>0.42-0.63</sub>Ti<sub>0.04-0.06</sub>W<sub>0.00-0.01</sub>)<sub>2</sub>O<sub>6</sub>.

Chemical composition of the columbites studied indicates that some pegmatites of Hruby Jesenik massif, for example that from Branna, show high degree of their Mn-Fe and Ta-Nb fractionation, while pegmatites from Kietlice in the Góry Sowie block and from Strzelin are poorly evolved. Two fractionation trends can be observed in Branna: I –

connected with an increase of Fe and Nb activity,  $\mathrm{II}$  – with an increase of Mn and Nb content.

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#### (Nb-Ta)-oxide minerals from pegmatites of the Owiesno-Kietlice area in the Sowie Mts block, Southwestern Poland

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The aim of our study was to determine chemical composition of Nb-Ta oxides in selected pegmatite locations in the Sowie Mts block, recognized in field outcrops in the Owiesno-Kietlice area. The Nb-Ta minerals studied belong to the columbite and the pyrochlore groups. They occur in veins, nests and lenses within metamorphosed pegmatites in association with common rock-forming minerals like quartz, plagioclase, muscovite, almandine, tourmaline, beryl, kyanite and andalusite.

Pegmatite samples have been observed in thin sections in both transmitted and reflected light. Chemical composition of (Nb,Ta)-phases was determined using a CAMECA SX-100 electron microprobe in the Inter-Institution Laboratory for Microanalysis of Minerals and Synthetic Substances at the Faculty of Geology, Warsaw University.

Euhedral, prismatic crystals of ferrocolumbite, reaching up to 100  $\mu$ m in diameter, sometimes show distinct, oscillatory zoning and are corroded. The ferrocolumbite formula is: (Fe<sub>0.56-0.63</sub>Mn<sub>0.34-0.39</sub>Mg<sub>0.00-0.01</sub>)(Nb<sub>1.73-1.99</sub>Ta<sub>0.01-0.26</sub>Ti<sub>0.01-0.06</sub>W<sub>0.01-0.04</sub>)<sub>2</sub>O<sub>6</sub>. A typical feature is extremely low value of the Ta/(Ta+Nb) ratio varying between 0.007 and 0.131, but typically increasing from the core to the rim of a grain. No distinct changes in Mn/(Mn+Fe) ratio varying between 0.351 and 0.410 are observed.

In one pegmatite sample, 10  $\mu$ m large, euhedral, isometric crystal of pyrochlore has been found. This pyrochlore has formula (Ca<sub>0.33-0.41</sub>U<sub>0.30</sub>Pb<sub>0.18-0.24</sub>Fe<sub>0.01-0.03</sub>Mn<sub>0.01-0.02</sub>)(Ta<sub>1.67-1.69</sub>Ti<sub>0.04-0.05</sub>Nb<sub>0.28-0.29</sub>)O<sub>6</sub>(O, OH, F)<sub>0.06-0.14</sub>, and can be classified as uranoplumbomicrolite. However, analytical totals distinctly lower than 100 wt% suggest that it probably is metamict and hydrated. This uranoplumbomicrolite is the first occurrence of microlite in Poland. Chemical composition of both the microlite and the ferrocolumbite suggest that studied (Nb,Ta)-pegmatites in the Owiesno-Kietlice area represent poorly evolved primitive LCT-pegmatites.

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## Textural and mineralogical evidence of the ocean floor metamorphism in the top part of the Ślęża ophiolite (SW Poland)

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The Ślęża complex situated in Lower Silesia represents one of the largest, most complete and extensively studied ophiolite in the Variscan Belt of Europe. Metabasalts, metadiabases and metagabbros in the eastern part of the Ślęża ophiolite occur in the form of lava covers, dykes, top parts of multiphase intrusions and, possibly, as top parts of magma chambers and deeper parts of the gabbro member with rooted dykes. A multiphase ascent of the tholeiitic magma and possible assimilation of earlier cooled and crystallized magma batches, at various depths, resulted in a great textural diversity of these rocks. Among aphanitic-textured rocks there are blastoporphyritic and blastoglomeroporphyritic types, while ophitic, subophitic, diabasic and intersertal textures occur within medium or coarse-grained gabbros. These features correspond to the "roof assemblage" described in detail in the Norwegian ophiolites.

Petrographic studies and electron microprobe determinations prove that these rocks were variably altered due to the hydrothermal, ocean floor metamorphism, which is common in the upper parts of ophiolites, and described by many authors. During the processes of ocean floor spreading, marine waters penetrated the cooling, fractured rocks of the Ślęża ophiolite and induced metamorphic transformations at various temperatures. Several modifications of hornblende formed from pyroxenes in the temperature interval of 750-550°C, being further changed into the actinolite hornblende and into amphiboles of the actinolite group below 450°C. Further cooling below 300°C resulted in the formation of chlorite and epidote-group minerals. The primary basic plagioclase changed composition into more acid, even reaching albite.

The alteration processes discussed spanned the range of the lower part of the amphibolite facies and the greenstone facies. Mineral assemblages formed at different conditions coexist in these rocks in the form of irregular, chaotic mosaics, and point to the lack of the facies equilibrium, the fact observed both in small samples and standard thin sections.

Relatively deep oceanic water penetration has been confirmed by isotope studies. The influence of oceanic water has also been indicated by hydrogen and oxygen isotopic compositions in rodingites within the lowermost, ultramafic member of the Ślęża ophiolite.
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# Tourmalines from the contact aureole of the Karkonosze granite (the case of Rędziny, Lower Silesia, SW Poland)

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Within dark-tingled andalusite-bearing hornfelses in the Rędziny quarry, numerous zoned crystals of tourmaline have been found. These tournalines show up to seven growth stages. The core (43-50% Sch, 42-48% Drv, 8-5% Ol) evolves toward varieties with lower amount of Al as a result of the  $[Na(Fe,Mg)](\Box Al)_{-1}$  substitution. Similar tends are visible in the zone II (47-52% Sch, 43-49% Drv, 2-4% Ol). In the zones III (52-45% Sch, 48-55% Drv) and IV (41-47% Sch, 59-53% Drv, 2-0% Ol) tournaline is still more Al-depleted and Mg-enriched. A tendency of Mg-contamination reaches a maximum during crystallization of the zone V (40% Sch, 56-60% Drv, 0-4% Ol). During the stages III-IV, the substitution at the X site is independent from the Mg(Fe).1 substitution at the Y site, and can be ascribed as  $Ca \square (2Na)_{-1}$  replacement. Simultaneous increase of Na and Al in the zone V suggests limited NaAl(CaMg).1 substitution. In contrast to internal zones I to V, tourmaline VI shows maximum content of Al (25-35% Sch, 41-48% Drv, 28-21% Ol) with a tendency of the Fe(MgAl)<sub>-1</sub> substitution, whereas tourmaline VII (34-38% Sch, 44-51% Drv, 18-11 % Ol) the (Mg,Fe)Al<sub>-1</sub> substitution. Both varieties are highly depleted of Si (~5.8 apfu) and distinctly of F (from 0.14 to 0.05-0.07 apfu). In the Fe-Al-Mg diagram, the tournalines I-V form well separated subsets within the field ascribed for tourmalines from metapelites and metapsamites not coexisting with Al-saturating phase. In contrast, the two outermost zones form subsets within the field ascribed for tourmaline associated with metapelites and metapsamites coexisting with Al-saturating phase. Biotite coexisting with the tourmaline crystals sometimes slightly replaces their mostouter zones. Its formation temperature ca. 669°C estimated on the basis of Ti content correspond to possible peak of the contact metamorphism. It seems that zones I-V formed probably during regional metamorphic event. The zones VI and VII have been grown during early stage of contact metamorphism, probably before or contemporary with biotite crystallization. This metamorphic event is related to intrusion of the Karkonosze granite.

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#### Stable isotope and fluid inclusion study of polymetallic mineralization in Jihlava Ore District (Czech Republic)

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In the Jihlava Ore District (Czech Republic, Moldanubicum) silver ores were exploited from the 13<sup>th</sup> century up to the 18<sup>th</sup> century. Ores form veins, mostly in N-S strike, up to several kilometers long and up to a few meters thick.

Two main types of polymetallic mineralization were distinguished based on their mineralogy and sulfur, carbon and oxygen isotope analyses: 1) High temperature mineralization (370-410°C according sulfur isotope thermometry) shows the source sulfur values between +3 and +5 ‰ CDT; sulfur was derived from metamorphic or granitic rocks of the Moldanubicum. The  $\delta^{18}$ O values of carbonates are relatively high (calculated  $\delta^{18}O_{fluid}$  up to +13 ‰ SMOW); the  $\delta^{13}$ C values are low (calculated  $\delta^{13}C_{fluid}$  about -10 ‰ PDB), indicating the presence of organic carbon in the hydrothermal process. The mineralization is composed of sphalerite, galena, pyrite, arsenopyrite; chalcopyrite, pyrrhotite and tetrahedrite-freibergite. The most common gangue minerals are represented by quartz and carbonates of Fe-Mg-Mn type (kutnohorite, Mn-siderite, dolomite-ankerite).

2) Mesothermal mineralization (230-340°C according to sulfur isotope thermometry) shows the source sulfur values between -3 and +3 ‰ CDT; the source of sulfur can be the surrounding rocks, too. Calculated  $\delta^{18}O_{fluid}$  values range from +4 to +6 ‰ SMOW for the main stage of mineralization. Calculated  $\delta^{13}C_{fluid}$  values are about -7 ‰ PDB; it corresponds to homogenized carbon of the Earth's crust. Sphalerite and galena are common in this type of mineralization; chalcopyrite, tetrahedrite, argentite, pyrargyrite are minor or accessory. Gangue minerals are formed by quartz, barite, dolomite-ankerite and calcite.

Primary and pseudosecondary aqueous inclusions were found in quartz, sphalerite and calcite of the second type of mineralization. The primary inclusions in quartz have mostly consistent liquid to vapor ratio (LVR=L/L+V) between 0,8 and 0,9, the values of homogenization temperatures (Th) ranged from 132 to 224 °C, temperatures of melting of the last ice crystal (Tm) were measured between -0,2 and -2,4 °C, corresponding to the salinity of aqueous solution from 0,4 to 4,0 wt. % NaCl equiv. The pseudosecondary inclusions in sphalerite revealed consistent LVR = 0,9, Th between 156 and 173 °C, and the higher salinity, from 8,1 to 11,0 wt. % NaCl equiv. (Tm = -5,2 to -7,4 °C).

The primary inclusions in calcite have variable LVR that was probably caused by long-termed maturation of the inclusions under relatively low temperature conditions (Bodnar et al. 1985). Homogenization temperatures were not measured; the salinity did not reach 1 wt % NaCl equiv. (Tm = -0.3 to -0.4 °C).

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#### A U-(Nb,Ta,Ti) oxide mineral from Podgórzyn – a preliminary report

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Pegmatites in the granitoid Karkonosze massif are commonly occurring rocks. Though it is estimated that most of them were removed together with the metamorphic cover and apical part of pluton by erosion, there are still common small sockets, veins or lenses of the pegmatites. Their bigger concentrations, formerly exploited for the ceramic industry, are situated near Jelenia Góra, Szklarska Poręba, and in Rudawy Janowickie Mts.

Research on pegmatites occurring near the Podgórzyn town, situated 5 km south of Jelenia Góra , in one of pegmatite bodies revealed the presence of a mineral, which in its chemical composition corresponds to liandratite  $(U^{+6}Nb_2O_8)$ . The pegmatite in which it occurs forms a socket of a few meters in size in porphyritic granite. The pegmatite mostly consists of quartz, K-feldspar, plagioclases, biotite and numerous accessory minerals: zircon, ilmenite, titanite, REE phosphates and Nb-Ta oxide minerals.

The mineral found forms a porous grain of irregular shape and dimension ca 60 µm (measured along the diagonal) and apparently replaces in part plumbopyrochlore. Chemical analysis made with an electron microprobe, beside the presence of U, Nb, Ta and Ti, showed also the presence of significant amounts of Bi (2.7-3.5 wt.% Bi<sub>2</sub>O<sub>3</sub>), Pb (1.5-1.7 wt.% PbO), as well as Si (1.7-1.9 wt.% SiO<sub>2</sub>) and P (0.40-0.45 wt.% P<sub>2</sub>O<sub>5</sub>). After calculations of the analysis, it turned out that the total cation content in the A-site is 1.45-1.48 apfu, which distinctly exceeds the theoretical 1.00. However in terms of the present knowledge on that mineral it should be treated as correct. On the other hand, the B-site cation population of about 1.8 apfu is relatively low compared to the theoretical 2.0 apfu, particularly that in the B position was also situated Si (0.17-0.19 apfu) and P (ca 0,04 apfu). The presence and a potential role of the two latter elements in that mineral structure is by far not explained. It is possible that part of Si is incorporated into the mineral structure and the rest of it is linked to metamictic domains, as it was found in case of pyrochlore. It is suggested that P can substitute for Nb in pyrochlores, so probably such a substition takes also place in that case.

Podgórzyn near Jelenia Góra is the first known occurrence of liandratite in the Karkonosze massif. Further research is necessary to determine a role of Si and P in the structure of this mineral.

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#### Genetic history of britholite from the Azov Zr-REE deposit (Ukraine)

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The Azov zirconium/rare-earths deposit is located within the laminated stock of quarz syenites (Melnikov et al., 2000a). The ore-bearing syenites should be considered as a final differentiate of a magmatic melt of subcrustal genesis (Melnikov et al., 2000b). The genesis of the Azov deposit includes formation of a residual syenitic melt enriched in Zr, REE, F, CO<sub>2</sub> and H<sub>2</sub>O. The high fluorine concentration enabled generating convective streams in the silica melt. The formation of the ore layers is due to the crystal accumulation. Zircon and britholite precipitation was synchronous at T=1100-950°C (Melnikov et al., 2000a). Thus, the main ore minerals are products of magmatic crystallization. After consolidation of rocks, britholite underwent drastic modification of its structure during slow cooling, in a result of which a new mineral was formed. The X-ray study and electron microprobe analysis have established that the britholite represents a mixture of several phases: primary Ce-britholite, bastnäsite, monazite as REE minerals, and secondary Y-britholite, quartz, fluorite as newly-formed minerals. SEM showed nanocrystalline sizes of bastnäsite and monazite. The most part of primary britholite exists in a metamict (amorphous) state. The lanthanides content in Ce-britholite is equal to 38-54% and that of yttrium to 2.5-3.5% Y<sub>2</sub>O<sub>3</sub>. The phosphorous content varies from 2 to 16% P<sub>2</sub>O<sub>5</sub>. The best inverse correlation of  $P_2O_5$  and SiO<sub>2</sub> contents agrees with the substitution according to the equation REE+Si  $\rightarrow$ Ca+P (Melnikov et al., 2007). It is important that primary britholite contains up to 1.2% ThO<sub>2</sub> and 0.15% UO<sub>2</sub> (Melnikov et al., 2007). Two factors affected the formation of britholite pseudomorphs: radioactive emanation of thorium and CO<sub>2</sub>-bearing fluid. During methasomatic replacement redistribution of lanthanides and yttrium took place. Sometimes a content of yttrium in secondary britholite increased up to 28% Y<sub>2</sub>O<sub>3</sub>. A monazite phase concentrated light REE and thorium (up to 5-7 wt.% ThO<sub>2</sub>) but preserved its crystalline state. Taking into account a content of pseudomorphs, an equation for a replacement reaction can be written as following:  $TR_{3-x}Ca_{2+x}[Si_{3-x}P_xO_{12}]F + \{(3-2x)CO_3^{2-} + 2(1-x)F^{1-}\} =$ (3-2x) TRCO<sub>3</sub>F + xTRPO<sub>4</sub> + { $(2+x)Ca^{2+} + (3-x)Si^{4+}$ } (fluid contents is in braces). It can be seen from this equation that the carbon dioxide-fluorine-water fluid is necessary for a transformation of britholite into bastnäsite.

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# A preliminary study of hydrothermal tourmaline from Lubietová deposit (Slovak Republic)

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L'ubietová is situated ~10 km eastern from Banská Bystrica in central part of Slovak Republic. L'ubietová is one of most famous copper deposit in Europe. Exploitation of copper ores lasted from the Bronze age to the 19th century. The Podlipa hydrothermal Cusulphidic deposit occurs in Permian greywacke and arkose rocks. Primary sulphidic mineralization in the Podlipa deposit is mineralogically very poor and composed of chalcopyrite, tetrahedrite and pyrite disseminated in thin quartz veinlets or surrouding rocks. Native copper and oxides of copper are rare. In the Podlipa deposit the mineral succession is as follows: Fe-carbonate  $\rightarrow$  Alpine paragenesis  $\rightarrow$  Cu-Fe-sulphides  $\rightarrow$  Cu-oxides  $\rightarrow$  secondary minerals. Minerals of Alpine stages are characteristic of thin quartz vein with dominating tourmaline and albite. Less frequently there occur chlorite, muscovite, hematite and accessory rutile, titanite, monazite-(Ce), xenotime-(Y), zircon and apatite.

The tourmaline studied forms black prismatic crystals grouped into radial aggregates. The tourmaline with quartz often forms comby textures. Chemical composition of this tourmaline suggests the predominant schorl component in the crystals. The Mg-rich schorl is almost chemical homogenous and its average crystallochemical formula is (9):  $(Na_{0.70}Ca_{0.05}\Box_{0.25})_{1.00}(Fe^{2+}_{1.51}Mg_{1.14}Al_{0.24}Ti_{0.07}\Box_{0.03})_{3.00}$ 

 $(Al_{5.95}Mg_{0.05})_{6.00}(BO_3)_3(Si_{5.92}Al_{0.08})_6O_{18}((OH)_{3.91},F_{0.09})_{4.00}.$ 

Two-phase fluid inclusions in the black schorl are very small (up to 5  $\mu$ m) and composed of a water solution and a vapour phase with average salinity 10.2 wt.% NaCl eq. (range: 3.4 to 14.4 wt.% NaCl eq.). Average homogenization temperatures of inclusions is 183.6°C (range: 122.3 to 226.9°C) and their average ice melting temperature is  $-6.6^{\circ}$ C (range: -2 to  $-10.5^{\circ}$ C).

We also studied white quartz associated with schorl. Fluid inclusions in quartz up to 5  $\mu$ m, are two-phase inclusions composed of water solution and liquid CO<sub>2</sub>. Salinity of water solution is ~4.4 wt.% NaCl eq. and varies from 2.7 to 6.8 wt.% NaCl eq. In quartz there were also found fluid inclusions composed of water solution and vapour phase with average salinity 18.66 wt.% NaCl eq.

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# Mineralogy of sulphides in mafic rocks of the Suwałki Anorthosite Massif, NE Poland

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The Suwałki Anorthosite Massif (SAM) is located in the Precambrian basement of north-east Poland and comprises mafic rocks, ranging from anorthosite, through norite and gabbronorite, to ilmenite-magnetite rocks. Sulphides constitute common accessory group of minerals in these rocks, although their content may locally reach 3 vol. %. This presentation summarises all existing data related to sulphide mineralization in the SAM and shows results of new EPMA and XRD study.

Up to now, in mafic rocks of the SAM, pyrrhotite, pentlandite, Co-pentlandite, chalcopyrite, cubanite, mooihoekite, haycockite, linnaeite, millerite, violarite, pyrite, marcasite, mackinavite, galena sphalerite, bornite, chalcocite, hessite, and clausthalite were recognised. Traces of Au-Ag, and PGM were also recorded (e.g. mernskyite, electrum, stützite, altaite, empressite, sopcheite, and telargpalite) Sulphides occur as droplet-like inclusions in magnetite, ilmenite, plagioclase and orthopyroxene, as well as irregular blebs between rock forming minerals (<0.5 cm in size). The sulphide blebs are overgrown by Mg-Al spinel rims that unequivocally show that these sulphides are related to magmatic stage. Some sulphides occur as thin veins and/or irregular concentrations revealing replacement textures. These document later hydrothermal events connected with development of pegmatite, micro-granite and quartz veins.

Mineralogical study reveals complex exsolution and replacement textures that document postmagmatic evolution of sulphides. The sulphide blebs and common droplet-like sulphide inclusions were originated probably due to liquation of sulphide melt which crystallized below 1100°C. Sulphide assemblages present in the SAM rocks are interpreted as developed during complex exsolution and recrystallization processes of the monosulphide solid solution (*mss*) and intermediate solid solution (*iss*), with the chemical composition close to Ni-pyrrhotite and chalcopyrite, respectively. The evolution of sulphides during cooling of the SAM can be described as follows: crystallization of *mss* (<1190°C), crystallization of *iss* (960-900°C), growth of coarse-grained pentlandite (<860°C), transformations of iss into chalcopyrite stable in low temperature (600-210°C), exsolution of flame-like Co-pentlandite (up to 13.4 wt. % Co) within pyrrhotite (<254°C), origin of cubanite-chalcopyrite intergrowths {200-210°C), growth of haycockite and mooihoekite (<160°C).

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



#### Effects of structural radiation damage on cathodo- and photoluminescence Emissions of minerals

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The decay of radio-nuclei may cause severe structural damage in minerals and other solids. This is in particular the case for alpha-decay events. Both the daughter nucleus (which is recoiled upon emission of a  ${}^{4}\text{He}^{2+}$  particle) and the alpha particle undergo elastic collisions with atoms in the material, resulting in atomic displacements. We have studied how structural effects can be probed using emission bands in cathodoluminescence (CL) and photoluminescence (PL) spectra.

In general, radiation damage results in changes of the crystal field around optically active centres. Low levels of radiation damage are therefore characterized by broadening of emission bands, indicating an initial disturbance of the short-range order. We have found that the Nd<sup>3+</sup> emission band at 872 nm ( ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$  transition) in the PL spectra of monazite from Moss, Norway, had a FWHM (full width at half band-maximum) of 4.9 nm, whereas after annealing the monazite had a FWHM of 2.9 nm. For the same sample FWHMs of 4.6 nm (damaged) and 2.7 nm (annealed) were determined for the Sm<sup>3+</sup> emission band at 608 nm ( ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$  transition). Similar irradiation-induced band broadening was observed in PL and CL spectra of other moderately damaged monazite, zircon, and fergusonite samples. Observations suggest that, after proper calibration, widths of emissions might be used as a simple means to estimate *in situ* the degree of radiation damage.

At elevated damage levels, the fine structure of groups of emission bands may be completely lost, which is then mostly accompanied by a significant drop of the emission intensity. In contrast, radiation damage (for instance in  $\alpha$ -quartz) may also create new luminescence centres and, thus, increase the emission intensity.

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#### Agates and geodes from the Khur Area, Central Iran

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Intensive volcanism during Eocene of the Central Iran caused the eruption of a huge volume of lavas and associated tuffs, which are intermediate to acid in composition. This is volcanism shows a continental margin volcanism, which is related to the subduction of the Neo-Tethys oceanic crust beneath the continental micro-plate of Central Iran. This long-term volcanism created one of important structural members of Iran Plateau with the NW-SE trend that is called the Urmia-Dokhtar volcanic belt. This volcanic belt hosts many of ore deposits and metallogenic provinces, as well as agate fields of Iran.

The Khur agate field is the most famous occurrence of agate and geodes nodules along through this volcanic belt that is located at in the southern border of the Great Kavir, Central Iran. The agate and geodes formed partly in the gas vesicles of the andesitic lava flows within a thick tuffaceous volcanic sequence. The relation between locally hydrothermal bentonitization of tuffs observed in places and agates that forming in the vicinity of lava flows supports a probable hydrothermaly genetic model for the latter.

The presence of goethite, calcite, aragonite, limonite, hematite, siderite and celestite as a low temperature assemblage, which find found beside chalcedony and quartz in nodules confirms approved the theory that silica was first removed from the andesites by low temperature hydrothermal solutions and then - after migration - reprecipitated as chalcedony and quartz in the vesicles of the lavas. It seems that hydrothermal formation of bentonite in andesitic tuffs, which took place occurred during a long-term volcanism, could be considered as a probable mechanism for providing bring out sufficient amounts enough of SiO<sub>2</sub> for agate- and geode-forming processes.

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# Microscopic and physico-chemical characterization of romanite from Colti, Buzau

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Amber became one of the most adequate substances for the interdisciplinary studies. For Romanian researchers, the main aim will be to clarify the geological origin of romanite and to establish if it represents an amber species or it is only one of the many european amber varities. The role of optical microscopy in the study of fossil resins is of prime importance. Apart from efficiency and commodity, it offers a precision grade comparable only with the chemical analyses, and at the same time it allows detailed mineralogical investigations of the resins and of the host-rock. Microscopic analysis may reveal, on a small scale, the genesis of an amber deposit. In Romania, a beautifull amber was exploited from the 19th century near Colti (Buzau County), on the Sibiciu Valley. The resin-bearing strata belong to the Oligocene in the Eastern Carpathian flysch. Having become a symbol of our country, the crud, brown-reddish amber named romanite or rumanite was exposed at the Universal Exposition in Paris, 1867. The systematical exploitation began in 1920, and between 1923 and 1925 more than 300 kg were extracted. By 1935 the exploration ceased. Between 1981 and 1986 the Ministry of Mines and Oil organized a systematical exploitation, but the extracted material was lost or became part of private collections (Ciobanu, Dicu 2005). Today amber of the Colti area is not for sale commercially. Diagenetic processes played a significant role in the creation of romanite. One of the most important consequences is the appearance of an internal organization tendency (Neacsu, 2006), proved by its weak anisotropy and the second one is represented by remineralizations in romanite (substitution of organic matter by anhydrite, albite and feldspar). In other situation, the organic tissue was replaced by resin. Two different romanite types exist: an older one, with distinct fissures, impregnated with organic material, and a recent one, lighter, which borders the previous one and penetrates its fissures. We highlight the anisotropy tendency of romanite, especially in the presence of organic material. The microscopic study seems to prove the crystallization tendency of romanite, raising thus the possibility of using X-ray diffraction as a diagnostic method for romanite.

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### Geochemistry and Nd isotopic signatures of metabasites from the Staré Město Belt, the West Sudetes

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In the Staré Město Belt (SMB), metabasites appear in a bimodal suite associated with felsic metavolcanic rocks and as small lenses of amphibolites in mica schists. Metabasites also occur within mica schists in the Javornik area, considered to be a part of the SMB displaced along the Sudetic Marginal Fault towards NW (Don et al. 2003). The SMB has been interpreted as a Cambrian-Ordovician continental rift sequence (e.g. Štípská et al. 2001; Don et al. 2003) embracing ocean floor basalts (Opletal et al. 1990) or E- to N-MORB and rarely low-Ti tholeiites (Floyd et al. 1996, 2000). Our geochemical results suggest that low-Ti tholeiites dominate in the SMB and they also occur in the Javornik area.

The tholeiites display low-Ti contents and fairly flat undifferentiated REE patterns. The low REE and HFSE contents in the tholeiites, similar or lower than those in N-MORB, and high Zr/Nb ratios and low Ti/V and Zr/Y values imply their derivation from a mantle source depleted more than that of N-MORB. The Nb anomaly, enrichment in Th and LREE, and high La/Nb ratios suggest mantle melts contaminated by continental crust in a magmatic arc setting. Floyd et al. (2000) consider the Sudetic low-Ti tholeiites as being derived from a lithospheric source contaminated by a sediment component in a continental rift setting.

In the SMB, the MORB-like tholeiites are distinguished from the low-Ti tholeiites by clearly higher Ti abundances, higher trace element and REE contents, and the lack of negative Nb anomaly. They are characterized by low Zr/Y, Ti/V and Ti/Y values, fairly flat, nearly undifferentiated REE patterns and slightly positive slope patterns on the spidergrams. These traits and  $\epsilon Nd_{(500)}$  6.3-9.6 suggest similarity to MORB-type basalts. The trace element contents and the La<sub>N</sub>/Yb<sub>N</sub> and Zr/Nb proportions indicate that the metabasites might originate from a variably enriched MORB-type mantle source transitional between N-MORB and E-MORB.

The low-Ti tholeiites from the SMB and the Javornik area are geochemically similar and have rather uniform mantle isotopic signature  $\varepsilon Nd_{(500)}$  5.2-7.2, which confirms the notion that the Javornik domain is a continuation of the SMB. On the other hand, the MORB-like tholeiites from the SMB are affined with the Stronie Group tholeiites and all are akin to the E-MORB-type basalts with little crustal contamination. The associated felsic metavolcanic rocks are *ca* 500 Ma old.

The similarities in both geochemical features and intrusion ages of the bimodal suite rocks in the eastern Orlica-Śnieżnik Dome and in the Staré Město-Javornik Belt allow to conclude that they all represent an extensive magmatic sequence developed in the same Cambrian continental rift-related system which probably evolved to a back arc setting. The latter suggestion still needs more support.

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#### Mineralogy and genetical study of hydrothermal siderite-quartzsulphidic veins in Jedl'ové Kostol'any, the Tribeč Mts (Slovak Republic)

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A small occurrence of ore veins occurs near Jedl'ové Kostol'any village, ~37 km NE of Nitra in the western part of Slovakia. The veins were discovered in the late 18th century and there were attempts to mine them in the 19th century. The hydrothermal veins in question occur in mylonitized Palaeozoic metamorphic rocks of the Veporic Unit. According to Polák (1957), the veins form a few lenses of WSW-ENE to W-E direction and dip 60° toward S-SE. The sizes of lenses are up to 20 m and their thicknesses up to 2.1 m. More characteristic are brecciated ore textures.

Predominant minerals are siderite, ankerite, dolomite, quartz, chalcopyrite and apatite-(CaF) which is typical mineral of this locality. Less common minerals are tourmaline (schorl and dravite), hydrothermal muscovite, hematite (var. specularite), cassiterite, rutile, zircon, xenotime-(Y), monazite-(Ce), cobaltite, pyrite, arsenopyrite, gersdorffite, tetrahedrite, galena, bismuth, cuprobismuthite and bismuthinite derivates. In Jedl'ové Kostol'any the mineral succession is following: Fe-carbonate  $\rightarrow$  Alpine paragenesis  $\rightarrow$ quartz-sulphides. There are few substages within the quartz-sulphidic stage: Ni-Co sulphidic  $\rightarrow$  quartz  $\rightarrow$  Fe-Cu sulphidsic  $\rightarrow$  Bi sulphosalts. The hypergene zone is less evolved and represented by goethite, malachite, azurite and erythrite.

According to detail mineralogical study and research of ore textures, hydrothermal monazite-(Ce) forms one generation. On the basis of electron microprobe dating the age of this monazite was estimated at  $83 \pm 9$  Ma (Th content is up to 6.8 wt.%.). The Ar/Ar ages of the hydrothermal muscovite which forms thin veins crossing carbonates are  $75.1 \pm 1$  and  $75.4 \pm 2$  Ma (Chovan et al., 2006).

An isotope study of siderite has provided the following data (average of two analyses):  $\delta^{18}O_{SMOW}$  +15.61‰ and  $\delta^{13}C_{PDB}$  -3.58‰. The average of two analyses of carbonates of the dolomite-ankerite series has provided the following values:  $\delta^{18}O_{SMOW}$  +13.25‰ and  $\delta^{13}C_{PDB}$  -2.22‰. The S<sup>r87</sup>/Sr<sup>86</sup> ratio of siderite from Jedl'ové Kostol'any (0.710020) together with others isotope data of the siderites from the Western Carpathians indicate strong influence of hydrothermal fluids by surrouding rocks.

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# Petrology and paleomagnetism of eocene to oligocene volcanic succession (Arctowski Cove and Point Thomas formation) from the King George Island – preliminary results

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The Eocene to Oligocene volcanic series comprise several, lava flows and volcaniclastic deposits of the upper part of the Arctowski Cove Formation and the underlying, younger Point Thomas Formation, both belonging to the Ezcurra Inlet Group (e.g. Birkenmajer 2001). Most of the lava flows are basaltic, rarely andesitic and dacitic in composition. The upper part of the Arctowski Cove Formation consists of sequences of lava flows with rare autobreccias at the top and laharic agglomerate interlayers, whereas the Point Thomas Formation contains the series of lava flows and pyroclastic deposits (tuffs with lapilli and bombs) as well as the tillite horizon (Birkenmajer et al. 2005).

The field work in Antarctica was carried out during the XXXIst Polish Antarctic Expedition to the Arctowski Station. Twenty two oriented samples were collected in the area of Italian Valley and Herve Cove These rocks dip about 20° towards SW.

Pilot samples were subjected to both alternating field (AF) and thermal demagnetization experiments. AF was more effective and thus the majority of samples was demagnetized using this technique. Demagnetization results were analysed using orthogonal vector plots, and the directions of the linear segments were calculated using the principal component analysis. The paleomagnetic conglomerate test was used to assess origin of the characteristic component. Magnetic mineralogy was determined from isothermal remnant magnetization (IRM) techniques, thermomagnetic analyses and scanning electron microscope (SEM) images. Anisotropy of magnetic susceptibility (AMS) was measured using a KLY-2 susceptibility bridge and resulting AMS fabrics were computed using the ANISO program.

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# Petrological analysis of the paint layers from the 15<sup>th</sup>-18<sup>th</sup> century icons from SE Poland

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The main aim of this work is petrological and geochemical analysis of mineral pigments from the icons of the 15<sup>th</sup>-18<sup>th</sup> centuries, collected at the Orthodox Art Department at the Castle Museum in Łańcut. The objects studied are a religious, historical and artistic phenomenon, being a part of cultural heritage of multinational Respublic of Poland. These paintings of high artistic value are representative of this regional iconographic style.

Samples of mineral pigments, grounds and lead white were collected from ten icons selected for the analysis. The samples were analysed by optical microscopy, SEM-EDS and INAA (instrumental neutron activation analysis) in order to determine the stratigraphy of art work and the identification of the pigments used. Twenty eight elements were selected for multi-parameter statistical analysis. The clustering analysis using STATISTICA (StatSoft) programme was carried out to identify the similarity degree of the objects analysed and the sources of the mineral pigments.

Together with commonly occurring pigments, such as vermilion (cinnabar), red lead, red iron oxide, orpiment, yellow ochre, lead white, chalk, gypsum, anhydrite and coppercontaining green, one unusual material was identified – lead tin yellow. Elemental analysis, especially trace elements analysis, carried out for lead white and earth pigments, allows establishing chemical patterns or "finger prints", which are characteristic of specific artistic workshops. Extensive research aimed at determining precise details on the painting techniques applied, as well as the age, origin and authenticity of the objects examined has brought the results that could be a basis for future restoration of the paintings.

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#### Human induced vivianite in the area of a north-east Hungarian chemical works

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Environmental geological survey of the chemical works situated in Northern Hungary has been performed since 1998. Up till now, more than 300 drillings of different depth as well as engineering geological soundings have been carried out in the area. In 2007 vivanite was found in a discrete part of the borehole ICE-113, drilled in the central part of the area of the chemical works.

The average elevation of the chemical works area is 94-95 m above the level of the Baltic Sea. In the area the thickness of the Quaternary formations covering the Pannonian terrain is about 150 m. This fluvial formation is highly layered; its lower part is dominated by coarser pebbly-sandy beds, whereas the finer sand-aleurite-clay layers are characteristic of the upper part. At the end of the Pleistocene, 1.5-2.0 m thick eolian sediment, such as sand, aleuritic (loessy) sand, coarse aleurite (loess), fine and coarse aleurite (infusion loess), accumulated and covered the fluvial fine-grained (clay-fine aleurite) sediments. Floor of the groundwater aquifer is formed by fine-grained aleurite. The upper part containing calcareous, limonite, and dendritic manganese concretions is yellowish brown; however, in general, it becomes grey and homogeneous below 5.0 m.

Vivianite was found in the grey, homogeneous clay bed at the depth 6.8-8.5 m in the drilling ICE-113; it appeared as lamellae along the fine laminae of the matrix or, rarely, as concretions of some mm across. According to soil mechanics studies, the vivianite was formed in the most massive part of the floor clay bed; the characteristic plasticity index is Ip = 32–40%, and the filtration coefficient ranges from 3.2 x  $10^{-11}$  to 4.9 x  $10^{-11}$  m/s. In the upper part of this bed, the characteristic plasticity index and filtration coefficient are Ip = 19 % and  $1.2 \times 10^{-10}$  m/s, respectively. At the same time, the characteristic filtration coefficient of the sandy groundwater aquifers is as low as  $2.2 \times 10^{-6}$  m/s.

Archive aerial photographs demonstrate that a coffered, earth-bedded reservoir for storing huge amounts of extracted plant debris is situated in the vicinity of the drilling ICE-113. Phosphate derived from decomposing biomass enters the groundwater, and then, according to the general SW path of the flow, is transported into and accumulated within the lowest permeability zone of the untouched bedrock. Therefore, the massive appearance of the vivianite in the drilling ICE-113 can be regarded, at least partly, as a result of a maninduced mineralogical process.

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# Bismuth sulphosalts from Kutná Hora, Czech Republic: new occurrence and data

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Several groups of complex Pb-Bi-Sb-Ag-(Cu-Fe) sulphosalts, previously unknown in Czech Republic, have been identified by WDS microprobe analysis in samples from hydrothermal vein mineralization of the Kutná Hora Ag-Pb-Zn ore district, central Bohemia, Czech Republic.

1. Lillianite homologues include both Bi>Sb members and Sb>Bi members (andorites) and show an extensive Sb for Bi substitution. The following phases were identified: gustavite, vikingite, treasurite, eskimoite, (Ag, Bi)-rich heyrovskyite, schirmerite, Bi-rich andorite IV, Bi-rich ramdohrite, Bi-rich fizelyite.

2. Kobellite homologues include izoklakeite (Sb>Bi) and giessenite (Bi>Sb).

3. Matildite-galena solid solution: all galenas associated with lillianite homologues in polished sections exhibit increased contents of Ag and Bi (max. 5.0 wt.% Ag and 9.7 wt.% Bi).

4. Other identified Bi sulphosalts include: aramayoite, cosalite, bismuthinite and Se-free ikunolite.

5. Bi-bearing Pb-Sb sulphosalts were detected: Bi-rich jamesonite (max. Bi/(Bi+Sb)= 0.26 or 15 wt.%, i.e. 3 out of 12 Sb atoms in the unit cell replaced by Bi), Bi-rich boulangerite (max. Bi/(Bi+Sb)= 0.12 or 5.2 wt.%), Bi-bearing semseyite (max. Bi/(Bi+Sb)= 0.02 or 1.12 wt.%).

The new data considerably extend the knowledge of chemistry and mineralogy of the Kutná Hora polymetallic deposit (Variscan age) in Czech Republic. The range of the  $Bi^{3+} \ll Sb^{3+}$ substitution in lillianite homologues with N = 4 has not been observed before and is exceptional in the world scale.

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# P-T conditions of extreme metamorphism of the Śnieżnik unit eclogites within the Orlica-Śnieżnik Dome

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Eclogites from the Śnieżnik tectonic unit within the Orlica-Śnieżnik Dome outcrop in the Bialskie Mountains SW of the Bielice village on NW slope of the Ruda Paprotnia Mountain and on the S slope of the Suszyca Mountain near Nowa Morawa. These rocks form small lensoidal bodies that are surrounded by orthogneisses. Eclogites are composed mostly of clinopyroxene, garnet, minor quartz as well as accessory rutile and epidote. These rocks had ultrahigh pressure metamorphic episode in their history. The eclogites originated at the expense of the calc-alkaline basic igneous rocks.

Garnets in eclogites from both the occurrences are composed mainly of almandine ~40 mol.% with pyrope and Ca molecule (grossular + andradite  $\pm$  uvarovite) of ~30 mol.% each. Garnets show distinct zoning with almandine increasing and pyrope decreasing rimwards.

Clinopyroxene is omphacite. The omphacite in the Bielice eclogites is richer in jadeite (47 mol.%) than in the Nowa Morawa eclogites (41 mol.%). In both the occurrences the blasts of omphacite are homogeneous and do not show any signs of zoning. Epidotes are zoisite, allanite and complex zoisitic-allanitic blasts.

The first author performed geothermobarometric analysis using garnet-pyroxene geothermometer (Powell 1985) and jadeite geobarometer (Holland 1980). The results of the analysis are as follows: 16-17 kbar and 700-750°C for mineral equilibrium in Nowa Morawa eclogites, and 17-20 kbar and 770-870°C for mineral equilibrium in the Bielice rocks. Estimated pressure shows the lowest value for the eclogite facies mineral equilibrium in the rocks analysed.

Taking into account the presence of quartz pseudomorphs after coesite which form inclusions in garnets and omphacites as well as topotaxial exsolutions of quartz in omphacite (Bakun-Czubarow 1995) which originated from supersilicic clinopyroxene during decompression, the second author estimated the possible P-T conditions of the metamorphism: 28-30 kbar and up to 900°C. These are conditions of extreme metamorphism. Coesite and nonstoichiometric supersilicic pyroxene are stable only under ultrahigh pressure, which occurs in the continental collisional zones at the asthenospheric depths. During decompression and uplift of eclogitic rocks from asthenospheric depths, coesite underwent transformation into quartz while supersilicic clinopyroxene topotaxially exsolved quartz needles.

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#### Evidence for episodic continental crust formation

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Models of continental crust formation based on trace element composition of depleted mantle and isotope composition of sediments are consistent with continuous increase of crustal volume through time with the most prominent increase observed in Late Archean and Early Proterozoic. In contrast, distribution of zircon crystallization ages and Hf model ages of zircon show several peaks through the Earth's history more consistent with episodic rather than continuous crust formation. At issue is the extent that the different episodes can be correlated between different continents and, therefore, whether they may represent global-scale episodes of continental crust formation.

Correlating Hf model ages is not straightforward because initial <sup>176</sup>Hf/<sup>177</sup>Hf in zircon may be hybrid due to magma derivation from a mixed source. Analyzing O isotopes allows us to distinguish between zircon grains having mantle-like  $\delta^{18}$ O and, therefore, non-hybrid <sup>176</sup>Hf/<sup>177</sup>Hf from those with elevated  $\delta^{18}$ O and hybrid <sup>176</sup>Hf/<sup>177</sup>Hf due to sediment assimilation.

So far coupled analyses of Hf and O isotopes in dated zircons are consistent with global crust formation episodes in the Early Hadean (~4.4-4.5 Ga zircons from Jack Hills and ~2.8-3.9 Ga zircons from the Slave craton), three closely spaced episodes in the Archean from ~3.8 to 2.7 Ga and an episode at ~2.0 Ga (Kemp et al. 2006, Pietranik et al., submitted). The last one is important also in the Variscan orogeny consistent with zircon composition from the Gęsiniec Intrusion (Sudetes, Poland) and Mid-German Crystalline Rise (Gerdes & Zeh 2006).

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#### Minerals of the phosphuranylite group: phosphuranylite, dewindtite and yingjiangite in a point of view of the new research

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Based on new research structure-chemical formulas of phosphuranylite (Demartin et al. 1991), dewindtite (Piret et al. 1990) and yingjiangite (Zhangru et al. 1990; Jingy et al. 1992) seem to be unsatisfactory defined for several reasons:

- Crystal structure of phosphuranylite proposed by Demartin et al. (1991) contains H<sub>3</sub>O<sup>+</sup> ions in interlayer due to electroneutrality. The presence of these ions was not proved either by IR and Raman spectroscopy (Čejka 1999; Plášil 2007; Frost et al. 2008) or by thermal analysis (Plášil, unpublished);
- The crystal structure of dewindtite (Piret et al., 1990) contains H<sup>+</sup> cations due to electroneutrality. The presence of these cations could not be inferred directly and was not proved by IR and Raman spectroscopy (Čejka 1999; Plášil 2007; Frost et al. 2006);
- Yingjiangite (Zhangru et al., 1990) seems to be only a variety of phosphuranylite. Based on XRD powder diffraction data, yingjiangite has the identical unit cell as phosphuranylite (Coutinho and Atencio, 2000).
- 4) All recently analysed by EMPA phosphuranylites, including the holotype specimen, contain potassium.

Conclusions:

1. Crystal structures of phosphuranylite and dewindtite should be refined implementing new bond valence parameters given by Burns (2005).

2. Phosphuranylite as a mineral species should be redefined with regard to the potassium presence.

3. Yingjiangite would be discredited as an individual mineral species (it is only synonym of phosphuranylite).

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# Alterations on the apatite and calcite surface buried in arctic soil (Spitsbergen): an AFM and SEM study

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This study is focused on direct observation of chemical weathering and biological activity on mineral surfaces in the newly forming arctic soil of the West Spitsbergen. Chemical weathering and soil forming processes associated with glaciers may affect several geochemical cycles including global carbon cycle, and as a result have negative feedbacks on the global climate. Study area are the foreland of the Werenskjöld glacier continuously retreating by several meters a year, and the incline of Mount Torbjörnsenfiellet. Several samples of freshly cleaved calcite and apatite had been buried in the soil for one year. Samples were analyzed with atomic force microscopy (AFM) and scanning electron microscopy (SEM/EDS)

Results of AFM investigation show changes observed on a calcite sample located about 500 meters from the glacier front. This sample recovered from Spitsbergen after 1 year of burial, and has been compared to the control that has never been exposed to glacier environment. The observed differences between these two samples include different types of weathered forms, various relations in topographic features including surface roughness and depth of weathered depressions, as well as types and quantity of microbioforms. The surface topography is difficult to compare between two different samples but at the scale of nanochannels ranging in the width from 1 to 5 nanometers, their depth increases on the average about 50% (from 0.3 to 0.45 nm) compared to similar nanochannels in the control sample. Microbioforms are about 70% less frequent on the sample recovered from Spitsbergen compared to the control sample. Irregular weathering surface structures are significantly more frequent on the sample recovered from soil. In some locations, hexagonal-like shapes might indicate initial stages of cryogenic calcite precipitation which might occur on the edges of columnar ice crystals.

Surface features of two grains of apatites were examined with SEM/EDS. Apatite 1 was buried in thick, mature tundra near the seashore and apatite 2 was located on the incline of Torbjörnsenfiellet about 300m above the sea level. Both were compared with the control. The surface of recovered apatites shows several similar changes. Dissolution marks include increase in general roughness of the surface and formation of rounded etch pits about  $1.5\mu$ m in size. Besides dissolution features, formation of mineral aggregates (about  $2\mu$ m in size) is apparent in both samples. The aggregates observed on apatite 1 are larger and more frequent than these on apatite 2. The EDS analysis reveals that Al and Si are the major components of the aggregates. The results indicate that the aggregates are autigenic aluminosilicates (kaolinite?) formed on the surface of apatite as a result of the activity of the soil solutions. Additionally, bacteria colonizing the surface of apatite 2 are apparent.

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#### Fluidal regime of mineral-forming processes in zone of influence of the Rakhiv-Tysynsk transverse fault of Carpathian (by mineralogicalparagenetic analysis and fluidal inclusions investigations data)

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Fluidal regime of mineral-forming processes within influence zone of Rakhiv-Tysynsk transverse fault of Carpathian was rhythmical and periodical while mineral-forming fluids (in particular mineral waters) penetrated along the fault into near-surface areas of the Earth forming in cycling manner carbonaceous travertine bodies of two-stages structure. The first level is situated under is situated under Earth surface directly in enclosed rocks in the form of shtockwerks (formed by carbonate streaks), while the second one was formed onto the surface has "tongue" form stretched downwards along slope and characterizes by sintered and biogenic (foliaceous, tabular and mossy)textures.

It was determined the following crystallization sequence of travertine formations principal minerals: milky-white calcite  $\rightarrow$  siderite  $\rightarrow$  manganous calcite  $\rightarrow$  arroyadite  $\rightarrow$  aragonite  $\rightarrow$  realgar  $\rightarrow$  yarosite  $\rightarrow$  dawsonite. Inclusions decrepitation temperature in calcite, manganous calcite, aragonite, realgar, yarosite has been determined. On the base of paragenetical analyses of travertine fluidal-dynamics peculiarities development in the fault during its historical retrospective was interpreted. Carbon-dioxide-carbonate fluids on the beginning of its development were changed into hydro-sulphate ones for the end etaps. At the present time Kvasiv deposit mineral water composition are following: NH<sub>4</sub> – 0.0018 (gr/l), K<sup>+</sup>- 0.0261, Na<sup>+</sup> - 0.4880, Mg<sup>2+</sup> - 0.0583, Ca<sup>2+</sup> - 0.1780, Fe<sup>+2</sup> - 0.0056, Fe<sup>3+</sup> - 0.0007, F<sup>-</sup> - 0.0005, Cl<sup>-</sup> - 0.5898, Br<sup>-</sup> - 0.0053, J<sup>-</sup> - 0.0009, SO<sup>2-</sup><sub>4</sub> - 0.0336, HCO<sup>-</sup><sub>3</sub> - 1.1346 and also carbon-dioxide (CO<sub>2</sub>) - 1.48 arsenious acid - (H<sub>3</sub>AsO<sub>4</sub>) - 0.010 et al.

In mineral waters composition as was ascertained periodically to the Earth surface were transported injurious for human health substances such as arsenic, sulphur, mercury and very likely strontium. So far as two water manifestations ("Kvasiv" and "Stepan") nowadays discharge onto surface directly in Chorna Tysa bed, it is obvious, that certain part of mineral water with injurious components admixture find oneself also in Chorna Tysa water. It must be noted that these components were accumulated in the river water with injurious components were accumulated in the river water with injurious components were accumulated in the river water with injurious components were accumulated in the river water during geological time that was testified by travertine mineral composition.

It is obvious, that these very unhealthy elements getting up onto Earth surface and river water influenced and continue to influence on the human health state and make worse ecological situation in the lower, from travertine manifestation, river flow. In spite of the fact that Kvasiv waters contain tolerant quantity of arsenic investigation of the natural source that makes worse ecological situation in the zone of Rakhiv-Tysynsk fault of Carpathian influence must be continued as far as is vitally important.

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# Sr, Ca, S - bearing monazite – (Ce) from the metamorphosed magnetite mineralization (Bacúch, Slovakia)

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The unusual high contents of S, Sr and Ca were determined in monazite-(Ce) from the metamorphosed magnetite mineralization in Bacúch (Veporic Unit, Western Carpathians). The magnetite mineralization hosted by mica schists and phyllites of the Jánov grúň complex is represented predominantly by quartz and magnetite replaced by hematite. Minor amounts of pyrite, sphalerite, pyrrhotite, native bismuth and cassiterite were also observed. The non-ore minerals are represented by tourmaline, the chlorite group minerals, biotite, K-feldspar, albite and zircon. The REE-dominated minerals include various types of monazite (Th-bearing, Nd-enriched, Ce-dominant as well as S, Ca and Sr-enriched), xenotime and hingganite. The REE minerals form usually small veinlets with quartz and albite. Monazite and xenotime were also found as matrix grains surrounded by magnetite or quartz.

The content of SO<sub>3</sub> in the S, Ca and Sr-enriched monazite–(Ce) reaches 10.66 wt.% with the contents of CaO and SrO being 4.59 and 7.42 wt.%, respectively. This is an effect of the strontium-enriched "clinoanhydrite" Ca,SrS(REE,  $Y_{)-1}(P,As)_{-1}$  substitution. The Ca or Sr could not enter the structure by the cheralite or "strontiocheralite" substitution Ca,Sr(Th,U)REE<sub>-2</sub> because of lack of Th. Sometimes uranium occurs in amounts up to 2.68 wt.% UO<sub>2</sub>. The thorium-rich members also occur with the content of ThO<sub>2</sub> up to 12.3 wt.%, but usually between 2 and 3 wt.%. Th-rich monazite does not contain S and its content of Ca is up to 1.31 wt.%; Th is incorporated by the cheralite substitution. Also Th-free monazite was found. All monazites are Ce-dominant with the content of Ce<sub>2</sub>O<sub>3</sub> from 24.47 to 33.61 wt.%, La<sub>2</sub>O<sub>3</sub> from 6.38 to 19.5 wt.% and Nd<sub>2</sub>O<sub>3</sub> from 8.91 to 21.92 wt.%. The content of other REE elements is very low, sometimes Pr<sub>2</sub>O<sub>3</sub> reaches up to 3 wt % and some analyses show up to 1.9 wt.% of Eu<sub>2</sub>O<sub>3</sub>. The S, Sr and Ca-enriched monazite contains up to 0.15 wt.% of common lead.

The chemical composition of hingganite is typical Y prevails over REE. However, the Nd dominant member also occurs. The X site is predominantly vacant (from 0.514 to 0.637 apfu) with the content of Fe from 0.363 to 0.486 apfu. The W site is occupied mainly by Y (from 0.443 to 1.113 apfu), less by REE (total from 0.695 to 1.431 apfu). The dominant REE cation is Nd (0.111 to 0.564 apfu), less Ce (0.058 to 0.256 apfu) and Sm (0.074 to 0.212 apfu). The content of Ca is very low, up to 0.113 in one analysis.

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# Complex crystal face control of nitrogen uptake during HTHP diamond crystallization

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Nitrogen is most abundant impurity in natural and synthetic diamonds. Distribution of nitrogen within a particular crystal can be non homogenous and often shows correlation with inner crystal structure. The fluctuation of nitrogen content usually interpret as change of crystallization parameters such as rate and mechanism of crystal growth, composition of parent fluid or melt. Properties of growing diamond surface as a factor of impurity uptake control is poor known.

We have studied nitrogen distribution within synthetic diamond crystals which were grown in Fe-Ni-C system at P=5.5 GPa and T=1450°C in IGM SB RAS (Novosibirsk, Russia) [Palyanov et al, 1997]. Total concentration of nitrogen was different for each experiment. The crystals show sectorial inner structure with clear growth sectors of faces of octahedron (111), cube (100), trapezohedron (311) and dodecahedron (110) (in order of occurrence). Nitrogen content and isotope composition was measured using high spatial resolution ion-probe ims1270 at EMMAC facility in University of Edinburgh (Scotland) [Harte et al, 1999].

Nitrogen abundance in sectors of 111 is highest and very close to initial abundance of nitrogen in the system. The nitrogen isotope ratio of sectors 111 is also equal to initial value. Sectors of faces 100 are depleted with nitrogen by factor of 2,5-4 in comparison with sectors of 111 for the same crystal. At the same time obtained  $\Box^{15}N$  values for sectors 100 are ca. 30 ‰ higher than initial composition. Part of the crystals formed by growing of face 311 shows "initial"  $\Box^{15}N$  values but abundance of the nitrogen is 10 times lower than that for sector of octahedron. No data was obtained for sector of face 110 because of its small size.

It is important to note that features described above are consistent for both studied crystals despite of difference in total nitrogen abundance. The difference in nitrogen isotope composition of sectors 111 and 100 also agreed with findings of S.Boyd, who get about 30‰ difference in  $\Box^{15}$ N between the sectors within a single synthetic diamond crystal [Boyd et al, 1988]. Obtained feature of different scale non equivalent uptake of both nitrogen atoms and isotopes during growth of particular crystal face is remarkable and deserve further extensive investigation. The features reported show evidently a tiny boundary between mechanisms of incorporation of atoms and isotopes of the same impurity.

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# Mineral infillings in cave bear (Ursus *spelaeus*) teeth and short bones from the Biśnik Cave (Częstochowa Upland, Poland)

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The bones and teeth studied come from the sediments of the Biśnik Cave. The sediments are represented by various clays, sands and loess and they have been forming since Odra glaciation until today. The bones and teeth were found in different layers, but mineral infillings were observed only in those from the loess layer.

The bones are recrystallized. Most of osteocyte lacunae and Haversian canals are not infilled with minerals, but locally secondary minerals, iron (hydro)oxides and calcite are observed. Iron (hydro)oxides (57-79% Fe<sub>2</sub>O<sub>3</sub>), with some admixture of manganese (0.05-0.64% MnO), occur in osteocyte lacunaes. Grains are up to few  $\mu$ m in size. Microcrystalline calcite coats Haversian canals or infills them entirely, and is also present between the bone trabeculaes. The presence of calcite was confirmed with X-ray diffraction.

In the teeth studied most of dentine canaliculi are filled with iron  $(0.15-6\% \text{ Fe}_2\text{O}_3)$  and manganese (0.35-78% MnO) (hydro)oxides.

The osteons in bone and dentine in teeth are cut by cracks, generally not filled with secondary minerals. They cut mineral infillings, proving that the latters formed earlier.

Various mineral infillings might reflect structural differences between bones and teeth. The presence of calcite infillings only in the loess sediment probably results from a higher content of calcite in that layer. There are no indications when the infillings formed.

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### Altered pyrite-bearing sandstones from Spitsbergen as an example of chemical weathering under the polar climate

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Pyrite-bearing sandstones, shales, siltstones and coal from the Todalen Mbr. of the Firkanten Fm. belong to the Van Mijenfjorden Group and crop out on the western slopes of the Endalen Valley (S Spitsbergen). Despite annual ten-month period of snow cover, yellowish to bright red weathering efflorescences are present on the sandstone surface. In addition to mineralogical description of the secondary phases, the objectives of this study were to evaluate the conditions of the weathering environment and to identify potential direction of the alteration processes. Goals were accomplished by means of standard mineralogical investigations (light microscopy, XRD, FTIR) combined with SEM-EDS-EBSD analyses.

The Firkanten sandstones are polymictic and composed mainly of quartz, alkali feldspar, mica and carbonates (siderite and calcite). Iron sulphide (pyrite), rutile and coal fragments are also common. Isometric pyrite crystals (up to 100  $\mu$ m in size) and framboids, uniformly dispersed within the rock, are associated with secondary minerals – mainly iron sulphates (both ferrous and ferric), gypsum and Fe oxyhydroxides. Reflected light micrographs as well as SEM images reveal widespread Fe sulphate covers on pyrite grains, which – by means of EBSD – have been structurally identified as melanterite. Ferric hydroxysulphates – predominately jarosite, as well as large gypsum crystals, are abundant within the rock, accompanied by crystalline and cryptocrystalline goethite. Fe sulphate pseudomorphs after gypsum were also found.

The precipitation of (hydroxy)sulphates and oxyhydroxides is controlled by the acidity and concentration of iron and sulphates in oxygenated water penetrating cracks and pores in the rock during polar summer. In the early stage of pyrite alteration, melanterite forms. Further oxidation leads to the formation of ferric phases. Alteration of feldspars and dissolution of calcite are the most probable sources of K and Ca for jarosite and gypsum, respectively. Such mineral association suggests rather early weathering stages driving most probably towards ferric oxyhydroxides and hydroxysulphates.

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# Mottramite, a Cu-Pb vanadate, from the Miedzianka - Ciechanowice polymetallic deposit (Rudawy Janowickie Mts, Poland)

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A polymetallic deposit of Miedzianka-Ciechanowice is situated within the Czarnów Schist Formation, which is mainly composed of mica-schists and amphibolites. This tectonic unit is a part of the eastern metamorphic cover of the Karkonosze granitic pluton. Two types of ores build this deposit: a massive magnetite-pyrite-pyrrhotite ore connected with skarns and ore veins with polymetallic mineralization.

In the weathering zone of the Miedzianka-Ciechanowice deposit, a number of secondary minerals (agardite-(La), bayldonite, brochantite, devilline, duftite, köttigite, philipsburgite, pseudomalachite, scorodite, wulfenite and other) occur.

On the dumps of the former Friederike Juliane mine, the authors found Zn-bearing mottramite, which occurs as yellow or green-yellow cryptocrystalline coatings on the surface of amphibolites. These coatings are built up of small (up to  $25 \,\mu$ m) tabular crystals. The crystals form characteristic rosette-like aggregates. On the waste pile of the old Einigkeit mine, the mottramite creates green massive accumulations within blue chrysocolla.

The chemical compositions (WDS method) have been recalculated in relation to  $\Sigma$ Me (Pb+Bi+Ca+Cu+Zn+V+As+P+Si) = 3 pfu. The average empirical formula of Zn-bearing mottramite from the Friederike Juliane mine is: (Pb<sub>0.93</sub>Ca<sub>0.06</sub>Bi<sub>0.04</sub>) (Cu<sub>0.62</sub>Zn<sub>0.27</sub>)[(V<sub>0.86</sub>,As<sub>0.09</sub>,P<sub>0.03</sub>Si<sub>0.11</sub>)O<sub>4</sub>](OH)<sub>0.67</sub> (n=12), whereas for mottramite from the Einigkeit mine is: (Pb<sub>0.88</sub>Ca<sub>0.11</sub>)(Cu<sub>0.94</sub>Zn<sub><0.01</sub>)[(V<sub>0.77</sub>,As<sub>0.10</sub>,P<sub>0.05</sub>Si<sub>0.15</sub>)O<sub>4</sub>](OH)<sub>0.82</sub> (n=8). Electron microprobe analyses reveal that the mottramite from the Friederike Juliane mine is enriched in Zn (3.89-4.49 wt.%), which correlates negatively with a Cu content (9.4-10.3 wt.%). These samples also show higher concentrations of Bi (1.03-2.51 wt.%) and lower of Ca (0.53-0.67 wt.%) in contrast to mottramite from the Einigkeit mine (0.00 wt.% and 1.07-1.28 wt.%, respectively). Deficits of major anions are supplemented by [AsO<sub>4</sub>]<sup>3-</sup> (0.01–0.11 pfu), [PO<sub>4</sub>]<sup>3-</sup> (0.02–0.06 pfu) and [SiO<sub>2</sub>]<sup>2-</sup> (0.07–0.17 pfu).

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POLSKIE TOWARZYSTWO MINERALOGICZNE



Uranospinite from the abandoned Podgórze uranium mine in Kowary (The Karkonosze Mts, Poland)

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Secondary uranium mineralization in form of uranospinite was found in uraninitebearing calcite vein in adit no. 15 of the abandoned Podgórze mine in Kowary. The mineral forms powdery, yellow coatings on calcite and rocks. SEM observations show that these coatings comprise typical tabular crystals, often rosette-forming. Analyzed (PXRD) sample contains both uranospinite and traces of metauranospinite. In addition, illite, quartz, a chlorite and calcite occur as impurities. Diffraction pattern is shifted in relation to available standards. The shift is connected with partial dehydratation of the research material (that could be caused both naturally or during preparation in mortar) and changes of mainly the *c* parameter that were observed by cell tuning in EVA v.11 program of Bruker AXS. Chemical data were obtained by microprobe method. The mineral is chemically pure. The contents of main constituents are variable (4.09 to 5.58 wt.% for CaO, 17.01 to 25.79 wt.% for As<sub>2</sub>O<sub>5</sub>, 58.60 to 65.75 wt.% for UO<sub>3</sub>). The UO<sub>3</sub> content is distinctly higher than the one reported by other authors for material from other localities (i.e. PALACHE et al. 1951). Phosphorus substitutes for arsenic in a very small degree, as the P<sub>2</sub>O<sub>5</sub> content is from 0.41 to 1.08 wt.%. The silicon content is negligible (up to 0.64 wt. %).

The crystallization of uranospinite is a recent phenomenon. This mineral crystallizes from mine water, which flows on the adit walls near the weathered calcite vein.

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# Vanadium and uranium secondary minerals from the Kletno deposit (Sudety Mts, Poland)

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The Kletno deposit is located in the Kleśnica stream valley, about 35 km SE from Kłodzko, in the Lądek-Śnieżnik Metamorphic Unit. The deposit is formed by two types of ore mineralization. The first type, represented by massive magnetite, occurs at the contact between metamorphosed sedimentary rocks (mainly marbles) and gneisses. Polymetallic, hydrothermal ore veins with rich mineralization (i.e. uraninite, fluorite, clausthalite, bohdanowiczite) are the second type and cut the massive magnetite ore.

The supergene zone of the Kletno deposit has been poorly recognized. Hitherto only few secondary minerals are known from there.

Beside chrysocolla, mottramite is the most common secondary mineral in the Kletno deposit. It forms thin green-yellow, yellow-brown or light green coatings on the surface of milky-grey massive quartz from hydrothermal veins. The mottramite coatings are very often mistaken for aggregates of secondary uranium minerals. The latter are built of small (up to 25  $\mu$ m), thin tabular crystals, whereas mottramite crystals form characteristic spherical aggregates. The chemical composition of the mottramite was determined by the electron microprobe method. The vanadium concentration varies from 17.79 to 17.73 wt.% V<sub>2</sub>O<sub>5</sub>. Arsenic (from 0.18 to 3.2 wt. As<sub>2</sub>O<sub>5</sub>) and phosphorus (from 0.11 to 0.37 wt.% P<sub>2</sub>O<sub>5</sub>) have also been recognized. A small amount of lead is replaced by calcium (up to 0,91 wt.% CaO). Concentrations of zinc and copper vary from 1.26 to 3.37 wt.% ZnO and from 2.49 to 5.53 wt.% CuO, respectively. A considerable addition of Si (from 2.49 to 5.53 wt.% SiO<sub>2</sub>) is present in the mineral examined.

Among the material found on old dumps of the Kletno uranium mine, some secondary uranium minerals have been recognized. One of them is kasolite. The mineral forms small (up to 20  $\mu$ m) tabular crystals, growing in small cavities in black fluorite. Semiqualitative chemical analyses (EDS) indicate a high concentration of calcium. This element partly replaces lead in the kasolite structure. Small amounts of magnesium and iron are also present.

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# Self-affine fractal statistics of igneous feldspar growth pattern transformed by a fluidinduced exchange reaction

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Alkali feldspar crystals chosen from the late Archaean TTG Closepet pluton have been investigated. The TTG suite crystallized from mixed felsic and mafic melts (Moyen et al. 1997). The feldspars have been collected from rocks displaying textures compatible with magma mixing. Trace element composition in each feldspar was analysed along several transects using LA ICP MS (usually 1200-1600 measurements along 1-1.5 cm). A 3D visualization combined with fractal statistics allow us to get insight into the mechanism of crystal growth. The 3D visualization of the trace element distribution shows that although the feldspars grew in similar heterogeneous magmas (e.g., mixed mantle- and crust-derived liquids) they display growth textures, which hardly can be explained by hybridization process. The feldspars are almost homogeneous. Mixing was then almost completed on the onset of feldspar nucleation and crystallization. Relatively small and irregular variation in the trace element contents makes the feldspar growth morphology patchy. This patchy pattern is developed on the basis of feldspar cleavage and seems to be caused by an exchange reaction with fluids. Fractal statistic, Hurst exponent or roughness exponent (H) have been determined for compatible trace element patterns along every one traverse in each crystal. The fractal statistics of the Closepet feldspars reveal that trace elements were incorporated chaotically into the grown crystals independently on the degree of mixing. The highest degree of chaos (H~0.30) appears in the feldspars grown from almost coherent magmas and it decreases during hybridization being always anti-persistent. The fractal statistics then can also be related to later fluid interaction with already crystallized phases and not to the dynamics of mixed magmas.

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### Cr spinels – indicators of mantle magma source in the Jeniniec-2 borehole

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Volcanic rocks from the Jeniniec-2 borehole are represented by andesites. The rocks are highly altered in the pumpellyite-actinolite and prehnite-actinolite facies conditions. Relict volcanic textures: porphyritic, amygdaloidal and, sometimes, ophitic are still visible. Primary plagioclase is completely albitized and sometimes contains rims of K-feldspar, occasionally it is replaced by pumpellyite as well. Mafic minerals are represented by pyroxenes: diopside and augite, which usually are replaced by mixed-layer chlorite/vermiculite, pumpellyite and quartz. The rocks often contain rounded grains of quartz and pieces of quartzite as well as garnet crystals, which indicate crustal contamination. As a rule, the more quartz is present in the sample, the more pyroxenes or pseudomorphoses after them occur.

Cr spinels are very rare in the rocks studied. They form very small rounded grains, few  $\mu$ m in diameter, and usually are grouped within phenocrysts (usually replaced by secondary phases) of plagioclase and pyroxene. The small size of crystals did not allowed to make more than one EMPA in each grain and contamination of analyses with surrounding minerals is visible (Si and Na are present). All spinels analysed can be divided into two groups: the first one (sample J2-22, lower part of the profile analyed) has Cr# ranging from 0.57 to 0.63, and the second one has Cr# from 0.70 to 0.75 (samples J2-9 and J2-10, upper part of the profile analysed).

Spinels rich in Cr (Cr# higher than 0.57) were described from petidotite, harzburgite and mid-ocean rift basalts and pyroxene-andesites from Caliornia (Barnes, Roedder 2001, and references there). The last mentioned rocks are probably close to the rocks from the Jeniniec-2 borehole. They are interpreted as a result of high degree of partial melting of the strongly depleted mantle. This thesis is confirmed by an increase in Cr# from older to younger parts of the volcanic rock sequence.

Metamorphic processes affected the Cr spinels. Released Cr was introduced into the structure of retrogressive celadonite, which is present in some pseudomorphs after pyroxene. The celadonite contains up to 1% Cr<sub>2</sub>O<sub>3</sub>.

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# Ferriallanite-(Ce) in graphite-bearing carbonatites from the Gremiakha-Vyrmes massif of the Kola Peninsula

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The minerals of the allanite subgroup are widespread in pegmatites of alkaline granites and syenites, but occur occasionally in carbonatites. They were described in the magmatic and hydrothermal carbonatites of the Kola Peninsula (Kapustin, 1971), Transbaikalia (Ripp et al., 2000), metamorphosed carbonatites of the Canary Islands (Ahijado et al., 2005), extrusive carbonatites of the United Arab Emirates (Woolley et al., 1991) and elsewhere.

For the first time ferriallanite-(Ce) was found on the Kola Peninsula in the graphitebearing calcite carbonatites of the Gremiakha-Vyrmes massif. The carbonatites of magmatic origin crosscut metasomatic albitites.

Ferriallanite-(Ce) is the only REE-bearing accessory mineral. It is associated with aegirine, biotite, albite, orthoclase, graphite, fluorapatite, ilmenite, titanite, zircon, prehnite, chlorite and sulphides. The similar assemblage was described in graphite-bearing calcite-biotite carbonatite crosscutting nepheline syenites from the Transantarctic Mountains of the southern Victoria Land (Cooper, Mellish, 2001).

Ferriallanite-(Ce) forms very small (up to 50  $\mu$ m), idiomorphic, brown crystals and rims on prehnite and chlorite. The chemical composition of grains is inhomogeneous, patchy. Single crystals are commonly zoned with respect to REE<sup>3+</sup> and Fe<sup>3+</sup>, with compositions corresponding to

allanite-(Ce):

 $(Ca_{1.07}Ce_{0.49}La_{0.41}Pr_{0.03}Nd_{0.13}Sm_{0.03})_{2.18}(Fe^{3+}{}_{0.62}Al_{1.59}Fe^{2+}{}_{0.71}Mn_{0.02}Mg_{0.04}Ti_{0.01})_{2.84}(Si_{2.84}O_{12.19})O(F_{0.01}OH),$ 

ferriallanite-(Ce):

 $\begin{array}{l} Ca_{1.34}Ce_{0.43}La_{0.38}Pr_{0.01}Nd_{0.09}Sm_{0.02})_{2.27}(Fe^{3+}_{0.75}Al_{1.16}Fe^{2+}_{0.64}Mn_{0.04}Mg_{0.07}Ti_{0.18})_{2.84}(Si_{2.90}O_{12.12})\\ O(F_{0.07}OH) \end{array}$ 

and allanite-(La):

 $(Ca_{0.97}Mn_{0.04}La_{0.44}Ce_{0.43}Pr_{0.02}Nd_{0.05}Sm_{0.02})_{1.97}(Fe^{3+}_{0.30}Al_{1.32}Fe^{2+}_{1.14}Mg_{0.06}Ti_{0.19})_{3.01}(Si_{3.02}O_{12.35})O(F_{0.07}OH).$ 

Chondrite-normalized patterns for ferriallanite-(Ce) from the Gremiakha deposit follow the general trend typical of carbonatites and differ from those recorded for ferriallanite-(Ce) from the alkaline granitic pegmatite (Kartashov et al. 2002).

The minerals of the allanite subgroup were formed in the late stage of carbonatite emplacement from postmagmatic, REE-rich hydrothermal solutions under high activity of  $SiO_2$  in the fluid.

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# Phosphatic overgrowths on zircon grains in Carboniferous sandstones

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Isotopic dating of sedimentation and/or diagenesis, despite the continuous advances in analytical techniques, is still underdeveloped compared to geochronology of igneous and metamorphic rocks. Authigenic phosphates precipitating on detrital zircon grains, typically xenotime and monazite in sandstones, have drawn attention due to their potential as U-Th-Pb chronometers. Many Precambrian samples have been successfully dated using this method, typically by presenting <sup>207</sup>Pb-<sup>206</sup>Pb age data. However, Palaeozoic overgrowths present more challenges, due to their lower radiogenic Pb contents.

This study forms part of a larger project testing the applicability of diagenetic phosphates to dating sandstones from the stratigraphically well- constrained Carboniferous basins – the Clare Basin of Western Ireland and the Pennine Basin of Northern England. Phosphatic overgrowths (xenotime and monazite) on detrital zircon grains have been identified in each of the 17 sampled sandstones from both basins. The overgrowths vary from euhedral to subhedral, with evidence of dissolution in some cases. The very small size of the overgrowths is the major analytical drawback: ~65% overgrowths are <3  $\mu$ m in diameter. The overgrowths were investigated in thin sections and conventional epoxy grain mounts using optical and scanning electron microscopy (SEM), electron probe (EP), and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

EP microanalyses caused significant damage of the overgrowths after focusing the electron beam for ~15 minutes on a 1-3  $\mu$ m spot. It revealed varied compositions for the overgrowths. Silica contents up to 1.6 wt.% are typical of authigenic phosphates. LA-ICP mass spectra acquired from traverses yielded mixed analyses of the zircon hosts, phosphatic overgrowths and epoxy due to the very small size of the pyramidal serrations. It is possible to distinguish the three phases in the mass spectra, however, no reliable geochronological analyses were obtained. Analytical challenges and future perspectives are discussed in the presentation.

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# Ilmenites from the Tertiary deposits relict between Rakovník and Velká Černoc (called Hlavačov gravels), Central Bohemia, Czech Republic

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Ilmenites from the "Hlavačov gravels", a locality situated near Rakovník (W of Prague), Central Bohemia, were studied by means of stereoscopic microscopy, conventional petrographic microscopy and SEM. These placer deposits of the Tertiary relict of a braided river contain mostly ilmenites (40–75 grain%), tourmaline (5–20 grain%), rutile (1–5 grain%), magnetite (1–10 grain%), andalusite (1–10 grain%), sillimanite and kyanite (1–5 grain%), zircon (1–15 grain%), leucoxene (1–15 grain%) and Fe-secondary minerals (0–70 grain%).

Ilmenite morphology is diverse, the shapes of grains varies from angular to subangular with homogenous texture. The ilmenites contain hematite lamellae, inclusions of apatite, pyrite and pyrrhotite, and some of them have caverns filled with clay. Triangular ilmenite network exsolved from a titanomagnetite can be sometimes observed. Chemistry of ilmenites shows a significant variability. There were found Mg-bearing ilmenites, Mg and Fe-enriched ilmenites, Mn-bearing ilmenites, pure ilmenites FeTiO<sub>3</sub> and ilmenites with Fe replaced by both Mg and Mn.

Many ilmenite grains are altered. The altered mineral phases include: pseudorutile, leucoxene and rutile. The mineral phases have been classified after Frost et al. (1983) at the basis of their Ti/(Ti + Fe) ratio: ilmenite <0,5, pseudorutile 0.5–0.7, leucoxene 0.7–0.9, rutile >0.9. Alterations are recognizable mostly along the rims and along the fissures. Another altered products create patchy grains due to different distribution of elements such as Fe, Mg and Ti. Leucoxene alterations can arise partly *in situ* in the places of weathering of the source rocks and partly after sedimentation of placer deposits.

Variability of ilmenite chemistry suggests different provenance of the placer deposits. The Mg ilmenites probably representes bazalts, pyroclastics rocks and bazaltic dykes of Neoproterozoic and Cambrian age from SE Barrandien. The Mn ilmenites are known from metamorphic rocks and mafic intrusive rocks. Trellis ilmenite grains were recognized from Barrandien subvolcanic rocks by Fiala (1977).

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## Felsic segregations within the eclogites of The Snieżnik Metamorphic Unit, West Sudetes

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The Śnieżnik Metamorphic Unit (ŚMU), built of variegated rocks metamorphosed in amphibolite-facies conditions, contains numerous eclogitic lenses, subjected to variously intensified amphibolitization. The eclogites from different localities display diversity in geochemistry and mineral composition, what is interpreted to be the evidence for varied protoliths and peak metamorphic conditions. Irrespective to location of the eclogitic lenses within ŚMU, their fresh, weakly retrogressed sectors frequently contain felsic segregations in form of veins, nests or intercalations. The segregations are several mm up to 20 cm thick. The felsic rocks form irregularly-shaped bodies or flattened zones parallel to foliation.

Mineralogical composition of the leucocratic segregations is heterogenous regarding localities. However, in all cases it indicates high-pressure metamorphic conditions for their origin. In the Międzygórze and Nowa Wieś eclogites, the blurred nests and sharply bordered veins have been observed. They are composed of Qtz, Grt, Phen,  $Rt \pm Zo$ , Omp, Pl(Olg), Ilm, All, Kfs, Py. The vein-like bodies occur also within the metabasites in Strachocin, having composition Qtz,  $Pl(Olg) \pm Grt$ , Zo, Ky, Phen, Bt, Rt. The Nowa Morawa eclogites contain up to 20 cm thick intercalations oriented analogically to weak textural anisotropy of the metabasites. Their paragenesis includes Qtz, Grt, Pl(Olg), Phen, Ky, Bt, Rt; additionally they comprise small, partially corroded grains of staurolite. Garnets in all the occurrences often display high Mg content, indicating HP conditions (Alm 37-63,  $Prp \ 6-32$ ,  $Grs \ 4-37$ ). Also white micas support this notion ( $Si \ p.f.u. \ 6.34-6.98$ ). Due to big spread of Mg-Fe proportions, the conventional geothermometry based on Grt-Phen pairs gave scattered results ( $620-820^{\circ}$ C for 15 kbar), however conformable with the results for eclogites.

The appearance of the felsic segregations usually suggests their migmatic origin in the eclogites-facies conditions. Generally, the felsites seem to be the product of anatexis of the eclogites; the veins represent an injected material, either from more distant parts of migmatised eclogites or their neighbourhood during HP episode. In case of the intercalations with staurolite, sedimentary protolith cannot be excluded.

Finally, the mineral composition of the HP felsic segregations, as well as the chemistry of garnets (higher Mg) and phengites (higher Si), distinctly differ from those features in the eclogite-bearing gneisses, suspected by some authors to register common, (U)HP metamorphism.

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### Deposit Rožná: the evidence of Pb-Zn mineralization and origin willemite and montroseite

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The Rožná deposit belongs to the Rožná-Olší uranium ore field and is situated in the north-eastern part in the high-grade Gföhl Unit of the Moldanubian Zone of the Bohemian Massif. Three stages of mineralization were described from Rožná (Kříbek, Hájek 2005). The first is pre-uranium quartz-sulphide and carbonate-sulphide mineralization, the second type is uranium mineralization and the third type is post-uranium carbonate-quartz-sulphide mineralization. The uranium mineralization comprises three types: carbonate veins, mineralized tectonic zones and so-called metasomatites.

Unusual Pb-Zn sulphide mineralization with uraninite-coffinite veins was found during mining at the 21st level. This sulphide mineralization is composed mainly of sphalerite. Pyrrhotite, pyrite and tetrahedrite are less common. The sulphides make up 50%, calcite is mine waste. Sphalerite is enriched in Fe (8.9 wt.%) and Mn (2.4 wt.%). Tetrahedrite is enclosed in galena and contains up to 34.5 wt.% Ag. Calcite is rich in SrO (0.5-2.3 wt.%) and ZnO (about 1.1 wt.%).

Younger uranium mineralization appears as up to 3 cm thick veins crosscutting the older sulphide. The veins have concentric structure. Coffinite 1 occurs the margin of the vein and is rimed by thin uraninite layer, whereas coffinite 2 forms the central part of the vein. Coffinite 2 differs from coffinite 1 by a higher content of CaO. Both the sulphide and the uranium mineralizations are altered. Sphalerite is replaced by newly formed willemite and Zn-rich chlorite. Willemite forms irregular aggregates and is contaminated by Na<sub>2</sub>O (1.2 wt.%) FeO (about 1 wt.%). Chlorite is zoned. Its central part is enriched in ZnO (up to 11.5 wt.%), whereas the margin is ZnO-depleted (5.3 wt.%). Uraninite is partly replaced by coffinite. Radial aggregates of montroseite appear additionally in coffinite. The presence of willemite, Zn-rich chlorite and coffinite indicates high activity of Si during the alteration.

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### The berlinite substitution in clinkers - environmental aspects

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The constant production of meat and bone meal (MBM) from cattle cadavers presents due to the regulations evoked by BSE a problem for many countries. Combustion is an attractive option of the MBM disposal. An environmentally safe way of such disposal is its use as an alternative fuel in rotary cement kilns, as the high temperature inside these kilns (close to 2000°C) guarantees 100% prion destruction. Combusting MBM in a cement kiln is a no-waste process, as the unburnt component – mostly Ca phosphate - gets incorporated into the clinker. The addition of P to the raw materials for clinker production presents a certain problem, as phosphorus influences the properties of the melt, the clinker's phase composition, the structure of clinker minerals, and their chemical composition. The experiments with MBM addition have shown that the P2O5 contents above 0.7 wt.% P2O5 in clinker increase the Ca<sub>2</sub>SiO<sub>4</sub> (belite) and CaO (free lime) proportions at the expense of  $Ca_3SiO_5$  (alite). As belite is less reactive than alite and free lime proportion above 5% is not acceptable for cement preparation, a series of experiments was performed to optimize the raw meal mix with respect to the resulting clinker phase composition. The amounts of the MBM ash addition ranged between 0.25 and 7.5 wt.%  $P_2O_5$ . The distribution of P among individual clinker phases was studied using an electron microprobe. It was found that in equilibrium-burned clinkers all P incorporates into the common clinker minerals and does not form any high-P phase. The contents of  $P_2O_5$  in belie and alite distinctly grows with its bulk content in the clinker. The interstitial phases (Ca aluminate and Ca ferrite) contain much less  $P_2O_5$ , mostly below 0.8 %. Phosphorus preferentially enters the structure of belite; already from the total content of 0.5 wt.%  $P_2O_5$ . The content of  $P_2O_5$  in belite exceeds more than twice that in alite. PO<sub>4</sub> substitutes in the structure of clinker silicates for Si in SiO<sub>4</sub> groups and Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> forms solid solutions with Ca<sub>2</sub>SiO<sub>4</sub> and Ca<sub>3</sub>SiO<sub>5</sub>. Besides this substitution, a certain portion of P appears to enter the belite as well as the alite structures via the berlinite substitution  $(2Si^{4+} \Leftrightarrow Al^{3+} + P^{5+})$ , known, e.g., from feldspars. The relation between  $P_2O_5$  and  $Al_2O_3$  contents in belie and alite appears to be linear within the whole studied range of  $P_2O_5$  contents (0.25–7 wt.%). The regression equation calculated from the results of spot analyses, AI = 0.214P + 0.053 (in a.p.f.u.), shows that the "initial" Al contents in belite is around 0.05 a.p.f.u. This finding led to experiments with raw meals enriched both in P and Al, which enabled the formation of alite even from mixtures with more than 3% P<sub>2</sub>O<sub>5</sub>, not occurring in clinkers from raw meals containing both Al<sub>2</sub>O<sub>3</sub> and  $Fe_2O_3$ .

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# Characterization of clay fraction of soils derived from granodiorites at the Sudety Mts. and the Foresudetic Block, SW Poland

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Granodiorites, except for granites, are most frequently occurring granitoid rocks in south-western Poland, but their exposures at the Earth surface are not extensive. There are only very few papers dealing with weathering processes and formation of clay minerals in soils derived from those parent rocks.

The aim of this work was to determine composition of clay minerals formed in soil profiles developed from granodiorites located in main geological formations of Lower Silesia (SW Poland): the Sudety Mts. and the Foresudetic Block, and to find to what extent the soil-forming processes affect composition of mineral colloids derived during weathering.

The objects of the investigation were shallow cambic soils located at upper parts of the hills formed by granodiorite intrusions of the Łużyce Massif and the Niemcza Zone.

Soil samples collected from different genetic horizons were dispersed in distilled water, then the clay fraction was obtained with a centrifuge. The only additional treatment of X-rayed samples included their saturation with glycol and heating at the temperature of  $550^{\circ}$ C.

X-ray diffractograms of soil horizons from the humus horizon to the parent rock detected dominating amounts of illite in all horizons and much smaller amounts of kaolinite and vermiculite. Those minerals are predominant components of the clay fraction obtained from different horizons of soil profiles located at the Niemcza Zone. The mineral composition of the clay fraction did not indicate significant differentiation from profile to profile, whereas the horizons collected from Łużyce Massif are also enriched in illite-chlorite interstratified minerals, montmorillonite and chlorite. There are also no clear differences in clay mineral composition along a soil profile.

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## Ammonium sulphates from burning coal dumps at Komló and Pécs-Vasas, Mecsek Mts., South Hungary

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In the surroundings of the Komló and Pécs-Vasas coalfields, on the burning dumps there were found numerous secondary sulphate minerals that formed by the decomposition of waste dump materials. Diversified associations of  $NH_4$ , Al, Fe, Mg, Ca and Fe sulphates, in various stages of hydration are the most abundant. They appear in porous or earthy masses, and encrustations consist of euhedral or anhedral crystals. These phases occur usually in close association. The nitrogen of the ammonium is provided by the decay of organic matter of coal. The identification of sulphates was made by X-ray powder diffraction, scanning electron microscopy aided with energy dispersive spectroscopy and inductively coupled plasma - mass spectrometry. Up to now, eleven ammonium sulphate species were identified in the Mecsek Mts. coalfield.

The most important ammonium-bearing sulphate is tschermigite. It mainly forms colourless to white, porous masses, or milimetre-size octahedra. Clairite (yellow tabular crystals with hexagonal outline), mohrite (yellowish tabular crystals), and boussingaultite (white tabular crystals) were identified in close asociation with tschermigite. Clairite was originally described in the cave environment (Martini 1983). Mascagnite often occurs in encrustations composed of thick tabular crystals, rarely associated with effemovite, koktaite and mohrite. Godovikovite appears as pale brown porous crusts with tschermigite and voltaite. Microcrystalline masses of sabieite were observed to occur together with mohrite and tschermigite. A jarosite-group mineral, maybe ammoniojarosite, occurs as powdery masses. Similar parageneses were identified from several other waste dumps (e.g. Žáček, Povondra 1988; Witzke, Rüger 1998)

The ammonium sulphates are often accompanied by other usual sulphates, such as alunogen, halotrichite, pickeringite, copiapite, gypsum, metavoltine, hexahydrite, kieserite, butlerite, voltaite, etc. Among them voltaite is very unusual, due to its variable cation substitutions. In the voltaite crystals significant amounts of  $NH_4$  substituting for K were identified in ICP-MS.

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### Gierałtów granulites – a vestige of an early Variscan ultra-high pressure metamorphism in the Olrica-Śnieżnik Massif, West Sudetes

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The eastern part of the Orlica-Śnieżnik Dome in the Sudetes, NE Bohemian Massif, belongs to key areas bearing evidence for UHP metamorphism in the Variscan Belt. The main lithologies cropping out in the area comprise amphibolite-grade Śnieżnik and Gierałtów gneisses intercalated with subordinate staurolite grade metasediments (the Stronie-Młynowiec Formation). These rocks host several inclusions of eclogites. Furthermore, in the Stary Gierałtów region a large body of interlayered felsic and mafic, retrogressed to a variable degree, ultra-high pressure (UHP) granulites has been recognized. In this study, we focus on evolution of metamorphic conditions revealed by the Stary Gierałtów granulites and on timing of UHP event using both conventional and isopleth geothermobarometry combined with Sm-Nd and Lu-Hf garnet geochronology.

Mafic granulite consists of clinopyroxene + kyanite + garnet + mezoperthite (former ternary feldspar) + K feldspar + plagioclase + quartz  $\pm$  biotite  $\pm$  amphibole. The peak metamorphic conditions were determined using conventional geothermobarometry at 28 kbars and 1010 °C, while decompression event was evaluated at 9.5 and 890 °C. Moreover, with the aid of an isopleth geothermobarometry, both P and T peaks were estimated at 30 kbar – 700 °C and 27 kbar – 930 °C, respectively.

Both mafic and felsic granulites collected from the same outcrop were subjected to dating. Sm-Nd dating of retrograded mafic granulite gave 340.1±4.1 Ma age, while Lu-Hf date, obtained for the same garnet fractions, yielded significantly older age of 374.1±1.5 Ma. Felsic granulite gave 320.6±2.5 Ma Sm-Nd age, while Lu-Hf date is 386.6±2.4 Ma. Sm-Nd date obtained for the felsic granulite, however, is about 20 Ma younger, what is rather unexpected since there is no tectonic discontinuity between the two lithologies. The interpretation of that age remains enigmatic. As expected in rocks crystallizing under high temperatures, major element zonation in garnet from mafic granulite shows typical diffusional pattern with equilibrated rims. This implies that the Sm-Nd ages reflect cooling. Lu-Hf geochronology shows more consistency. Both samples seem to point to an isotopic closure at c. 375-386 Ma. Since Lu-Hf system is believed to have higher closure temperature than Sm-Nd, the Lu-Hf ages are interpreted as representing time close to the metamorphic peak.

Thus, our PT results and geochronological studies indicate that investigated mafic granulite recorded two distinct metamorphic episodes characterised by early Devonian UHP metamorphism followed by ca. 40 Ma younger decompression stage.

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## Molecular modeling simulations and some of their applications in mineralogy and geochemistry

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Possibility of investigations of geochemical and mineralogical processes at the atomic scale is very tempting. Nowadays scientists are equipped with very sophisticated apparatus (e.g. electron microscopes), which offers possibility of performing studies at the atomic scale of resolution. However, there exist an alternative approach – molecular modeling, which can help to understand experimental results and even deal with problems where these empirical methods fail.

Molecular modeling comprises various computer simulation methods, which differ in the theoretical approach lying behind them. In this presentation two of these methods will be covered: quantum mechanics (QM) and molecular mechanics (MM).

QM considers energy and movements of particular electrons and nuclei in molecules. Using this approach it is possible to predict structures, physical properties as well as chemical reactions. We used QM in studying relative thermodynamic stabilities of some organic molecules found in oils - phenyldibenzothiophenes (Ph-DBTs). Using QM it was also possible to evaluate reactions, which these molecules could undergone during diagenesis.

MM describes molecules as balls (atoms) connected by springs (chemical bonds). This is much more simplified approach and, therefore, it does not cover the same fields of applications as QM. However, due to its simplicity and less computer time demands, MM can be used in the studies of much bigger systems, such as for instance clay minerals. We were interested in investigating the way in which a polymer – polivinylpirrolidone (PVP) - adsorbs on surfaces of clay minerals. Using the MM approach it was possible to choose the most likely conformation of polymer on the clay surface. Theoretical diffractograms were calculated on the basis of the structures obtained and compared with experimental ones.

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# Vanadinite from Stanisław quarry (Izerskie Garby Zone, Sudetes, Poland)

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Mineralization in the Stanisław quarry is associated with the Izerskie Garby dislocation zone, located within hornfelses and gneisses of the Karkonosze-Izera Block (Lewowicki 1965). Quartz is the predominant mineral filling, whereas the fluorite-apophyllite-quartz-calcite-stilbite-chlorite association is of hydrothermal origin (Kozłowski 1978). Vanadinite was found in a quartz-fluorite-stilbite vein cutting the hornfels. Fluorite is main mineral of the vein. It forms pale green octahedrons up to 1 cm in size, coated by quartz. Stilbite forms prismatic crystals up to 0.5 cm long. They are pale brown to orange with semi-vitreous to pearly lustre. Vanadinite was observed on the surface of a fracture cutting hornfels. It is the last mineral in the association. Vanadinite forms aggregates of hexagonal prismatic crystals up to 0.1 cm long. It shows orange colour and resinous to diamond lustre.

Electron-microprobe analyses and BSE images were obtained using a Cameca SX 100 apparatus in the Inter-Institutional Laboratory of Microanalysis of Minerals and Synthetic Substances at the Faculty of Geology, Warsaw University. The average crystal chemistry formula of vanadinite from the Stanisław quarry is  $Pb_5[(VO_4)_{2.85}(AsO_4)_{0.10}(WO_4)_{0.05}]Cl_{0.95}O_{0.05}$ . The vanadinite shows sectoral structure, caused by variable V, As and W substitutions in its structure.

As vanadinite is a typical secondary mineral in the oxidation zone of lead deposits, it is suggested that galena or other primary Pb -minerals may occur in the hydrothermal system of the Izerskie Garby Zone.

Wall-rock silicates might be the source of V. The Stanisław quarry is the first vanadinite occurrence in Poland.

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### New occurrences of wulfenite in the Polish Sudetes

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Occurrence of wulfenite in the Sudetes was first reported by Websky in 1851 (*fide* Traube 1888) from the polymetallic ore deposit in Miedzianka (formerly Kupferberg) near Jelenia Góra.

We report here on new occurrences of wulfenite in pegmatite from the Paszowice granite quarry (the Strzegom-Sobótka granitic massif) and in the abandoned galena mine in Lutynia (the Śnieżnik metamorphic massif).

Orange bipiramidal crystals, up to 0.2 cm in length, of wulfenite from Paszowice were collected from the intragranitic pegmatite. Wulfenite occurred in small cavities between aggregates of clinozoisite prismatic crystals, close to partially altered galena crystal (2 cm in size). Some of the wulfenite crystals are twinned.

Wulfenite from Lutynia was found in samples of quartz-galena veins within mica schists of the Stronie Metamorphic Series. Galena is strongly altered. Main products of its alterations are white cerussite and pale-green pyromorphite. Wulfenite forms tabular to bipiramidal crystals on quartz and pyromorphite.

Electron-microprobe analyses of wulfenite were performed using a Cameca SX 100 in the Inter-Institutional Laboratory of Microanalysis of Minerals and Synthetic Substances at the Faculty of Geology, Warsaw University. The average crystal chemistry formulae of wulfenite from Paszowice and from Lutynia are  $Pb_{0.99}(Mo_{0.96}W_{0.05})O_4$  and  $Pb_{0.99}(Mo_{0.98}As_{0.02}W_{0.01})O_4$ , respectively. Wulfenite from Paszowice is zoned and the zoning is enhanced by the variability in Mo and W concentrations. Wulfenite crystals from Lutynia reveal growth sectors with variable concentrations of Mo, As, and W. Wulfenite from the both localities originated as a by-product of hydrothermal alteration of galena.

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# Y, REE-rich zirconolite from the Skalna Brama pegmatite near Szklarska Poręba (Karkonosze Massif, Lower Silesia, Poland)

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REE-bearing minerals from the Skalna Brama pegmatite were reported by Websky (1865), Traube (1888) and Gajda (1960 a,b). The pegmatite is located within granite of the Karkonosze Massif. It forms lens-like body up to 5 m thick with internal structure comprising from the rim inwards: granitic and graphic zone, blocky K-feldspar and massive quartz core. The rock-forming minerals of the pegmatite include quartz, microcline, oligoclase, biotite. Ilmenite, chlorite, hematite, gadolinite, fergusonite, monazite, zircon, xenotime, uraninite, pyrite and arsenopyrite are accessory minerals.

Zirconolite was found as aggregates of needle-like branching crystals up to 4 cm long and up to 0.2 cm wide in massive pink microcline and grey quartz. It shows brown to black color and semi-vitreous to resinous lustre.

A sequence of crystallization was determined using BSE images, performed by an ESEM-XL 30 TMP (Philips/FEI) SEM equipped with an EDS (EDAX) detector (Faculty of Earth Sciences, University of Silesia, Sosnowiec). Zirconolite is a first mineral in succession. Fergusonite, monazite, xenotime and zircon crystallized later. EMPA were carried out using a Cameca SX-100 (Masaryk University, Brno). Due to the metamict state, the analysis yield low totals (90-95 wt.% oxides). The composition of studied mineral shows a strong deviation from the stoichiometric composition  $CaZrTi_2O_7$ . The Ca and Zr are very low (0.07 and 0.58 apfu, respectively) and replaced by Y (0.60 apfu), REE (0.32 apfu; HREE>LREE), Sc (0.17 apfu) and U (0.12 apfu). The lowered Ti (1.23 apfu) is compensated by Nb (0.21 apfu), Ta (0.09 apfu) and Fe (0.36 apfu). Further studies are necessary to elucidate substitution mechanisms and the structural parameters.

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## Unusual mineral assemblage in pockets of Ca-skarns at Moravské Bránice near Brno (Czech Republic) and its genetic implications

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An unusual association of skarn minerals with large amounts of microcline and albite occurs in pockets of small calcic skarns. These skarns form small bodies in a lens of pyroxenic gneisses rich in plagioclase ( $An_{25}$ - $An_{39}$ ), which represent the remnants of the host rocks of the proterozoic Brno massif granitoids near Moravské Bránice village, South Moravia.

Several stages of evolution of pocket associations have been deduced from the chemistry and position of the pocket minerals. (1) Fine-grained diopside-hedenbergite, which is omnipresent in the pyroxenic gneisses, survived the skarnization process and is nowadays dispersed throughout the skarn bodies and their pockets. (2) The oldest skarn minerals are represented by older grossular garnet, which formed together with large amounts of quartz and some vesuvianite. (3) A younger generation of pocket minerals features garnet, richer in andradite component, which is present as thin overgrowths on older garnet crystals in pockets or as small individuals. This garnet grew contemporaneously with a younger generation of hedenbergite, which overgrows older diopsidic pyroxene in pockets. (4) The last process, which was also restricted to pockets, was most probably an infiltration of low-temperature hydrothermal fluids similar to fluids of Alpine paragenesis. In addition to the formation of the youngest minerals (mainly microcline, albite, ferropargasite), the fluid also caused an alteration of older skarn minerals, mainly older garnet cores, the composition of which is closer to the grossular end-member, while the younger garnet overgrowth remained intact.

A concept for the younger stages of evolution of the mentioned skarns features among others: the possibility of a significant time gap between the evolutionary stages (3) and (4); the "drying out" of the system in the final stage of evolution, causing the preservation of the andradite-richer garnet generation in pockets; a surplus of SiO<sub>2</sub> in all fluid types.

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### Sorption of the volatile hydrocarbon compounds by Oligocene clay

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Hydrocarbon compounds evaporating from petroleum spills can be transported through the unsaturated zone. Hydrocarbons sorbed to the mineral phase play an important role within natural attenuation and hydrocarbon migration processes. Potential sorbents for volatile hydrocarbons are carbonates, clay minerals and organic carbon. In order to investigate natural attenuation processes, a special column experiment was conducted in a laboratory. Volatilization and sorption features of 39 hydrocarbon components have been measured on dry soils during the long-time experiment. Volatilized compounds were analyzed using gas chromatography; whereas sorption processes were investigated using mainly gas chromatography and X-ray diffraction methods. The results of sorption of volatile compounds are presented here.

The liquid gasoline used in the experiment consisted of compounds up to  $C_{19}$  at the initial period. The heavier hydrocarbons have been enriched in the liquid phase, due to a volatilization of hydrocarbons having smaller carbon numbers. Depending on the mineral composition of geological samples, 6,6-11,6% of the starting quantity of liquid hydrocarbon volatilized during the first three weeks. After half year and one year 27,7-37,2% and 37,7-51,1% of the liquid fraction volatilized, respectively. Quantity of volatilized hydrocarbon compounds reached 50,0-65,0% at the end of the experiment.

The investigated clay was collected from the Kiscell Clay Formation, which is a well studied and widely spread formation in the surroundings of Budapest. Clay mineral fraction of this clay contained smectite, chlorite, muscovite, illite, kaolinite, quartz, calcite and dolomite. Carbon numbers of the sorbed components were in range of 7 to 14. The average preferential hydrocarbon sorption order was the following: xylenes, C<sub>9</sub>, toluene, C<sub>10</sub>, C<sub>8</sub>, C<sub>11</sub>, C<sub>12</sub>, nC<sub>7</sub>, benzene, C<sub>13</sub>, MeCH, CH, C<sub>14</sub>. Quantity of the sorbed hydrocarbons increased with decreasing distances from the source, changes in a composition also occurred depending on variable distances. For example, in the case of 50 cm height column, composition of the top layer consisted of mainly xylenes (24%), toluene (19%), C<sub>9</sub> (19%), C<sub>8</sub> (13%) and C<sub>10</sub> (13%). In the top layer of 200 cm height column, the order of main compounds was as follows: C<sub>11</sub> (24%), C<sub>10</sub> (23%), C<sub>9</sub> (15%), C<sub>12</sub> (13%) and xylenes (8%). Comparing the results of different analytical methods (GC and XRD) an adsorption is presumably the main sorption process.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



# Characterization and re-evaluation of the "Apulian Marbles" (district of Fasano and Caranna: south-eastern Murge; district of Trani and Andria: north-western Murge, Apulia, Italy)

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The research regards the "Apulian Marbles" study, widely used in ancient times and even now, to list a Technical Database file.

Mineralogical, petrographical, geochemical, paleontological, mechano-physical analyses and ageing tests of the carbonatic litotypes (limestone and bio-chalky sandstone) from the area of Fasano-Caranna and Andria-Trani were carried out to evaluate a correct utilization of each material in a relation to the trade and to the resistance to the external agents.

These results are necessary for restoration and preservation of historical and artistic buildings constructed of the Apulian carbonatic litotypes.

In fact, it is well-known that a serious restoration of monuments should not begin if each feature of the materials, used for building purposes, had not been studied. Today, like in the past, lack of knowledge on characteristics of the materials used increases an active deterioration of the restored monuments.

The Apulian studied litotypes are: *Cocciolato, Mano fradicia, Filetto rosso, Caranna* (District of Fasano-Caranna); *Serpeggianti imperator, KF* e *Minerva, Mano grossa, Taddone,* and *Massello* (District of Trani-Andria). For all samples the following analyses were carried out:

NORMAL recommendation:

petrographic, X-ray diffraction (Seifert-Pad 4; 40 KV, 30 mA), SEM, AFM, EPMA, and X-ray fluorescence (XRF) analyses; loss on ignition (LOI):  $(H_2O)^+$  and  $(H_2O)^-$  determination, CO<sub>2</sub> content (calcimeter method), atomic absorption spectrometry to determine Na, K, and Ca; NH<sub>4</sub>, SO<sub>4</sub>, and chloride determination: qualitative and quantitative determination of insoluble residue (IR) after powder chemical attack with acetic acid.

#### - ASTM normative:

inhibition test, specific weight determination, propagation speed of elastic waves, weight density determination, porosity determination, bearing strength uniaxial determination, Poisson coefficient, modulus of elasticity in shear, ageing test.

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



# Lazulite and Sr-, Ba-, Ca-, and K-rich phosphates-sulphates from quartz veins in the Tribeč metaquartzites, Slovakia: compositional variations and evolution

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The phosphate-sulphate mineralization hosted in quartz veins in Lower Triassic metaquartzites occurs over large area in the Tribeč Mts., Western Carpathians, Slovakia. The mineralization comprises lazulite, Ba-, Sr-, Ca-, and K-rich phosphates-sulphates and barite, in an association with muscovite, hematite, rarely rutile, chlorite and tourmaline. The most widespread lazulite forms up to 10 cm large blue aggregates in massive quartz. EMPA shows a relatively uniform composition with Mg/(Mg+Fe)=0.85-0.93 and locally elevated F contents (max. 0.26 apfu). The Mössbauer spectroscopy reveals 11-30 % Fe<sup>3+</sup>/Fe<sub>tot</sub> in lazulite. Goedkenite-bearthite s.s. shows the highest known Sr contents worldwide: Sr/(Sr+Ca)=0.67-0.71; whereas REE, Mg and Ba contents are low. Lazulite is replaced by Ba-, Sr-, Ca-, and K-rich phosphates-sulphates: gorceixite, goyazite, crandallite, svanbergite, jarosite and a phase close to  $(Ba,K,Sr)(Fe^{3+},Al)_3[(OH)_6(PO_4)(SO_4)]$ composition (Ba,Fe,P,S-phase). Gorceixite exhibits more restricted compositional variations, between gorceixite-goyazite and gorceixite-crandallite s.s.: Ba/(Ba+Sr)=0.73-0.99, Ba/(Ba+Ca)=0.78-0.99. On the other hand, the Sr and Ca-dominant phosphatessulphates show wide compositional variations and complex solid-solution series between goyazite-crandallite and svanbergite-woodhouseite with Sr/(Sr+Ca)=0.16-0.99 and (P-1)/[(P-1)+S]=0.07-0.97. The K and Ba-dominant phosphates-sulphates occur along jarosite-Ba,Fe,P,S-phase line with Ba/(Ba+K)=0.07-0.56, Fe/(Fe+Al)=0.55-0.99, P/(P+S)=0.14-0.57 and elevated Sr and Ca (up to 0.24 and 0.12 apfu, respectively). The textural relationships and deformation microstructures indicate an origin of the phosphate-sulphate mineralization during Alpine low-grade metamorphic-hydrothermal overprint. The minerals crystallized from aqueous solutions of the H<sub>2</sub>O-NaCl-MgCl<sub>2</sub>-CO<sub>2</sub> system, with 17.2-19.8 wt.% NaCl eq. at minimum temperatures of 180-250 °C. The dominantly epizonal values of the Kubler index of muscovite (mean= $0.21\Delta^{\circ}2\Theta$ , st. dev.=0.028) point to the peak metamorphic temperatures of >300 °C.

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# Tectonic meaning of the jadeite-blueschist, ophiolite, and radiolarite exotics in flysch-mélange succession of the Western Kaczawa Complex (the Sudetes)

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The chaotic rock association containing jadeite-blueschists, ophiolite-type basites and ultrabasites and radiolarites as well has recently been described as the Jędrzychowice succession (Wajsprych, Achramowicz 2003). It is situated in the westernmost part of the Western Kaczawa Complex at the boundary zone with the Görlitzer Schiefergebirge. Geochemical characteristics of jadeite-blueschist indicates these lavas as basanitetrachybasanite alkali basalts extracted from enriched mantle source WPB, having no signs of crustal contamination, which may ascribe them to the oceanic plateau (Achramowicz, Wajsprych 2004). The presence of the ophiolite-type ultramafic rocks is noted by numerous chromite grains in flysch-type mélange matrix. The gabbroic rock, forming a large exotic body, shows a coarse-grained cumulate structure, with large plagioclase crystals and idiomorphic Fe-Mg minerals. An alteration of the latter to chlorite, serpentine, talc, titanite, calcite and opaque minerals indicates serpentinization as the mechanism of alteration (Wajsprych, Achramowicz 2003). The andesite-type rocks have been found as large blocks of massive and pillow lavas and volcaniclastics. The chlorite + zeolite + prehnite + quartz + calcite paragenesis of these lavas indicates a very low grade metamorphism ( $\leq 1$  kbar and ~200°C), not exceeding the degree of alteration of the wildflysch matrix (Wajsprych, Achramowicz 2003). Another exotics are radiolarian cherts. Some of them disclose the middle Famennian age (Wajsprych et al. 2006).

Summing up, the Jędrzychowice succession can be interpreted as a mélange of some rock-sets representing different tectonic domains: (i) - subducted oceanic crust (the jadeite-blueschist); (ii) – a normal oceanic crust (ophiolite-type, unmetamorphosed basites and ultrabasites) with its (iii) – volcano-sedimentary cover (unmetamorphosed, radiolarian-bearing mudstones and cherts with andesite-type massive and pillow lavas and volcaniclastics, which additionally disclose (iv) – an island arc domain. Concluding, the domains identified seems to offer a common and cohesive model of pre-Late Famennian intra-oceanic subduction followed by post-Famennian exhumation.

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# New mixed-framework silicates: (Rb,Cs)<sub>9</sub>Y<sub>7</sub>Si<sub>24</sub>O<sub>63</sub> and isotypic Rb<sub>9</sub>Y<sub>7</sub>Si<sub>24</sub>O<sub>63</sub> - syntheses and topology

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The two novel title compounds were obtained as part of a detailed study of the system  $M^{1+}-(M^{2+}-)M^{3+}-\text{Si-O}$  ( $M^{1+}=$  Na, K, Rb, Cs;  $M^{2+}=$  Sr, Ba;  $M^{3+}=$  Sc, V, Cr, Fe, In, Y, Yb), with a focus on new microporous mixed-framework silicates containing octahedrally coordinated  $M^{3+}$  cations.

The new silicates were grown using the high-temperature flux-growth technique (MoO<sub>3</sub>-based flux mixtures in Pt crucibles in air;  $T_{\text{max}} = 1150^{\circ}$ C, cooling rate 2 K/h,  $T_{\text{min}} = 900^{\circ}$ C). The crystal structures have been determined from single-crystal intensity data. Both compounds crystallise as prismatic to needle-shaped, colourless crystals in space group  $R\overline{3}$  with a = 28.819(4) / 28.799(4), c = 13.916(3) / 13.864(3) Å, V = 10009(3) / 9958(3) Å<sup>3</sup>, Z = 6, R(F) = 4.99 / 6.44%, respectively. They represent a novel structure type with microporous character.

The asymmetric unit of  $(Rb_{5.33}Cs_{3.67})Y_7Si_{24}O_{63}$  contains four mixed Cs/Rb sites, four Y, eight Si and 21 O atoms. The connection of three Si(1)O<sub>4</sub> and three Si(2)O<sub>4</sub> tetrahedra results in a six-membered, corrugated ring; however, this "ring" is in fact a spiral composed of corner-sharing SiO<sub>4</sub> tetrahedra parallel to the *c*-axis. The Y(3)O<sub>6</sub> and Y(4)O<sub>6</sub> octahedra are linked together via a common edge. The remaining corners are all shared with SiO<sub>4</sub> tetrahedra. Approximately parallel to [111] run two different, irregular channels hosting the Cs and Rb atoms. One of these channels in  $(Rb_{5.33}Cs_{3.67})Y_7Si_{24}O_{63}$  is defined by a seven-membered ring with a diameter of about 2.77 x 3.85 Å, delineated by six SiO<sub>4</sub> and one Y(1)O<sub>6</sub>.

The only significant difference in  $Rb_9Y_7Si_{24}O_{63}$  is that the Rb(1) site is split into two sites, with a Rb(1A)–Rb(1B) distance of 1.058(14) Å. Additionally, the two split sites, as well as the Rb(3) and Rb(4) sites, are slightly to strongly disordered. The relatively high R(F) value may be due to some unrecognised twinning feature.

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### Gypsum-rich black crust on the Libiąż dolomite in Krakow: Differences in dry and wet deposition dominated environments

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Black gypsum-rich crusts which developed on the Libiąż dolomite (Middle Triassic) and were exposed to weathering in a relatively highly polluted atmosphere in Krakow (Southern Poland) were studied. Samples were collected in two contrasting environments – from a wall subjected to rainwater washing (a wet deposition and dry deposition environment) as well as from a wall sheltered from rain (a dry deposition environment).

Gypsum with subordinate dolomite is present in black crust from both environments. Platy gypsum crystals form rosette intergrowths. In the black crust from the wall sheltered from rainwater loosely packed agglomerations of gypsum crystals are also noted. In samples from the wall sheltered from rainwater washing soil-derived dust (quartz, micas, feldspars) and anthropogenic dust is present along with a small amount of calcite and whewellite. Authigenic, non-stoichiometric dolomite ('protodolomite') is present in samples from a rainwater-washed surface whereas authigenic calcite is present in samples obtained from surfaces sheltered from rain. This difference suggests that dissolution of the dolomite rock occurs on rainwater-washed surfaces. Whewellite originates from the metabolism of microorganisms.

Concentrations of various elements are different in black crusts formed on rainwaterwashed surfaces and those sheltered from rainwater. Their average values are: Fe - 0.45 and 0.84 wt%; Pb - 573 and 1401 ppm; Zn - 1033 and 2232 ppm; Ni - 27 and 83 ppm; Mn - 872 and 1743 ppm; Cr - 225 and 426 ppm respectively. Higher concentrations of these elements in the black crust found on wall surfaces sheltered from rainwater are related to a significantly higher amount of dust which is removed by rainwater from these washed surfaces.

The values of  $\delta^4 S_{CDT}$  (1.88-5.75‰) and  $\delta^{18}O_{SMOW}$  (4.99-8.60‰) in gypsum from both groups of samples are very similar.  $\delta^4 S_{CDT}$  values are very close to those measured in rainwater in Kraków and generally are slightly higher than in the gypsum from black crust developed on the Jurassic limestone. The isotopic composition of S indicates that fuel combustion is its dominant source. The lack of differences in the O isotopic composition can suggest that sulphate ion from aerosol is dominant in the gypsum in both environments.

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# The enclaves from Kośmin granodiorite (Niemcza Zone)-their origin and varieties

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Granodiorites occurring in the Niemcza Zone (NE Bohemian Massif, SW Poland) represent igneous activity at ~340 Ma (Oliver et al. 1993) during the Variscan orogeny in Europe. Hornblende–biotite granodiorite from the Kośmin quarry is medium–grained and porphiritic and exhibit magmatic foliation and lineation defined by elongated aggregates of hornblende and biotite. Two main types of enclaves are hosted by the granodiorite: (1) dominating enclaves of monzonitic to granodiorite composition and (2) scarce and variable metamorphic enclaves. The granodiorite is crosscut by synplutonic lamprophyric dykes.

Our main aim was to characterize the dominating enclaves and their origin. The enclaves are widespread in the SE part of the quarry. They vary in size from ~4 to ~90 cm in diameter with those 20–30 cm large being the most abundant. The smallest, centimeter–sized ones occur in groups and sometimes grade into schlieren. The enclaves have ovoid, globular and lenticular shapes. Their foliation and lineation are similar to those in granodiorite. A continuous range of enclaves occur from fine-grained monzonitic ones to porphyritic granodioritic ones, strongly resembling the hosting granodiorite. Only occasional are monzodioritic, medium-grained enclaves rich in mafic minerals.

All enclaves consist of plagioclase, biotite, pyroxene, amphibole with alkali feldspar and quartz occurring in the enclaves resembling the host. Accessory minerals are apatite, opaque minerals, zircon and titanite. Some enclaves are rich in feldspar porphyrocrysts, probably derived from the surrounding granodiorite.

The whole petrological spectrum of enclaves occurring in the Kośmin quarry is consistent with mixing between partially crystallized granodioritic and dioritic magmas. The suite of enclaves is an excellent example of mixing process that most probably took place before injection of the dioritic magma into the granodioritic one.

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



# Amphibole compositional trends in alkaline rocks from the Polish Western Carpathians

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In the western part of the Outer Polish Carpathians, between Bielsko-Biała and Cieszyn, an occurrence of shallow sills of alkaline rocks can be observed. Their mineral composition is relatively simple; the main phases are olivine (Fo<sub>90-75</sub>), clinopyroxene (diopside-hedenbergite-aegirine), dark mica (phlogopite-biotite-annite) and amphibole (kaersutite). Among the light minerals, feldspar and nepheline are dominant. The fractionation of olivine, Ti-rich diopside, kaersutite and plagioclase caused that the derivative magma ultimately reached the stage of nepheline syenitic composition.



Fig. 1. Compositional variation of amphiboles in the the system Mg-(Fe<sup>2+</sup>+Mn)-Na.

Two main compositional trends of amphiboles were found in the alkaline rocks studied (Fig. 1). In picrite and picroteschenite, amphiboles range in composition from kaersutite and ferrokaersutite through Mg-hastingsite, Mg-katophorite to richterite (evolution at low  $f_{O2}$ ). Amphiboles in teschenite sills range from kaersutite-ferrokaersutite through hasingsite (early magmatic stages) to taramite/katophorite (theralite teschenite, trend 1a) or Ferrichterite and arfvedsonite (diabasic teschenite-trend 1b at high  $f_{O2}$ , late magmatic stages).

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#### Fe-skarn mineralization in Saheb area, NW of Iran

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Saheb iron deposit is located in the northeast of Saghez in Sanandaj- Sirjan geotectonic zone, NW of Iran. Saheb Fe-skarn developed along the contact of Saheb intrusive body with carbonatic rock. Intrusive body, which is composed of granodiorite to monzodiorite, intruded into volcanoclastic rocks and Permian limestones (Routeh Formation). Most structures in this area have East - West trending and mineralization follows this trend. 70 polished sections and 30 thin sections were analyzed petrographically. We also analyzed 10 samples by XRF for petrological purposes. The results show that major rock forming minerals of the intrusive rocks are plagioclase, K-feldspar, amphibole, quartz, biotite. The minor minerals include garnet, clinopyroxene, apatite and chlorite. The main alteration minerals are sericite, epidote, clay minerals, chlorite and calcite. Based on mineralogical and geochemical analyses these are I-type calc- alkaline intrusions.

The main ore minerals are magnetite and hematite which are formed by magnetite oxidation and decrease by increasing of depth ore mineralization. Fe-mineralization consists of lenses, up to 10 m thick. The 50 trench samples were analyzed for S, P, Fe (t), FeO, and 280 diamond drilled hole samples were analyzed for S, P, FeO,  $Fe_2O_3$ , Au, Cu,W, Sn, CO, MnO, SiO<sub>2</sub>, and CaO. All samples were analyzed by General Wet Chemistry method (GEN). The results showed average content of Fe: 51.72%, Cu: 0.35% and Au: 0.038 ppm for these samples. This ore deposit has a total reserve of 3.2Mt with an average grade of 50 percent Fe (total).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



# Chromites from serpentinites of lelova Metamorphic Sequence (South Carpathians, Romania)

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The Ielova Metamorphic Sequence (IMS) is located in the south-western Romania. As part of the South Carpathians, the IMS represents the most western area of Danubian Domain in the region. Lithologically, it consists mainly of amphibolites and gneisses with garnet and biotite. Isolated lizardite-dominant serpentinites bodies crop out in its western part.

Chromites within serpentinites from the IMS were studied from mineralogical, morphological and chemical points of view by means of optical microscopy, back scattered electron imaging (BSE) and energy dispersive spectrometry (EDS). The grains show signs of strong alterations.

The core of the relict chromite crystals is characterized by a geometrical arrangement of chlorite lamellae forming a network of narrow channels crosscutting mostly at 90° and 120°. This is due to the pseudomorph replacement of Mg-Fe-rich twin lamellae of the primary chromite. Magnetite-dominant rims, with a non symmetrical arrangement of chlorite veinlets, surround the chlorite-chromite structure. Clinochlore is also identified, mostly confined to the chromite relicts, but can also be related to large primary magnetite grains.

The unaltered parts of chromites have a low Mg content (<5%), as shown by EDS. The decrease in the Fe content is associated with an increase in Al, while the Cr content remains constant. This chemical composition indicates a chromite-hercynite solid-solution with low magnesium content.

These characteristics point to an initial, ordered chemical zoning of the chromite crystals, with uneven distribution of Mg, which determined chlorite growth during alterations.

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### Loparite decomposition in the late stage of evolution of alkaline melt: evidence from titanosilicates melting experiments

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Loparite  $(Na,Ce,Ca)_2(Ti,Nb)_2O_6$  is a principal ore mineral of the Lovosero rare-metal deposit. Our study has demonstrated that loparite may be replaced by other minerals during late stages of high alkaline magma evolution. We have recognized seven mineral assemblages formed after loparite (Kogarko et al. 2002). All of them contain titanosilicates (mosandrite, lamprothyllyte, barytolamprophyllite) and phosphates (monazite, Sr-apatite, vitusite, belovite) or silicophosphates (vuonnemite, lomonosovite, stenstrupine).

Melting of three titanosilicates was experimentally studied. It has been founded that they melt incongruently: lamprophyllite melts with formation of a melt, nonstechiometric tausonite((Sr<sub>1-x</sub>Na<sub>x</sub>)TiO<sub>3-x/2</sub>), rutile (TiO<sub>2</sub>) and freudenbergite (Na<sub>2</sub>Fe<sub>2-x</sub>Ti<sub>6+x</sub>O<sub>16</sub>); barytolamprophyllite melts with formation of a melt, tausonite, Ba-Fe titanate and titanosilicate of strontium and barium; lomonosovite melts incongruently with the formation of perovskite-lueshite solid solution, freidenbergite and two immiscible liquids: silicate and phosphate (Na<sub>x</sub>Me<sup>2+</sup><sub>y</sub>PO<sub>4</sub>) melts. The tausonite and perovskite-lueshite solid solution are the loparite analogs. The experiments show that melting of titanosilicates may be a model of loparite decomposition.

The separation of the lomonosovite components into salt (phosphate) and silicate parts allows us to assume that silicophosphates can be formed through interaction between loparite, immiscible silicate and salt (non-silicate) melts. This interaction may be schematically described as:

 $\begin{array}{c} 2NaMe^{2+}PO_{4}+2(Na,REE)TiO_{3}=Na_{3}PO_{4}+REEPO_{4}+2Me^{2+}TiO_{3}.\\ Na_{3}PO_{4}+Me^{2+}TiO_{3}+nSiO_{2}+H_{2}O_{2}O_{4}(Me^{2+})_{5}(PO_{4})_{3}(OH)+Na_{x}Ti_{y}Si_{z}O_{(x/2+2y+2z)}\\ Na_{3}PO_{4}+REEPO_{4}=Na_{3}REE(PO_{4})_{2}\\ nNa_{3}PO_{4}+Na_{x}Ti_{y}Si_{z}O_{(x/2+2y+2z)}=Na_{x}Ti_{y}Si_{z}O_{(x/2+2y+2z)}*nNa_{3}PO_{4}\\ \end{array}$ 

Variations in composition of minerals in the pseudomorphs after loparite are probably due to the evolution of residual melt.

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# Chemical composition of the glass phase from melting crucibles (Mečová Street, Brno)

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Two medieval melting crucibles from Mečová Street in the historical centre of Brno were studied in order to determine the nature of raw materials and the technological aspects of their production and use. The samples were analysed using optical microscopy and SEM.

Heterogeous glass was found in the first sample. The glass forms a thin layer on the surface of the crucible. The major components are  $SiO_2$  (50.39–67.38 wt. %),  $Al_2O_3$  (12.01–27.34 wt. %) and CaO (5.0–19.6 wt. %). The restitic crystal phases are formed by the long columnar to needle-like augite and wollastonitte. It also contained relicts of primary quartz and plagioclase. Fe and trace amounts of Zn, Cu and Ti were the only found metal phases. Traces of Zn and Cu in the glass indicate possible melting of copper or brass.

The second sample includes also heterogenous glass, which appears mainly on the surface. This glass is depleted in SiO<sub>2</sub> (34.96-41.12 wt. %) and rich in CaO (16.71-36.37 wt.%). The contents of alkalies ( $K_2O$  0.59–5.55 wt. %, Na<sub>2</sub>O 0.91-2.63 wt. %) are similar to the first sample. The glass contains traces of Zn + Cu and Co and Ni as well. On the contrary, this melting crucible is full of drops or coatings of metal copper and its secondary minerals. Fe-rich spinel, garnets and kaliophilite are restitic phases.

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# To the problem of phase heterogeneity of quartz of sedimentary and metamorphic genesis

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Raw quartz from deposits of different sedimentary and metamorphic genesis is a traditional stuff for building materials and composite binder production. Mineralogical investigations of this raw material usually consists of determining its chemistry and grainsize characteristics. We have measured a variation of strength properties of composite binders manufactured on the basis of fine-ground Portland cement, when quartz of different deposits, localized in sedimentary and metamorphic rocks, was used (Strokova et al. 2007).

To define the reasons of the variation of strength properties, XRD investigations of quartz were conducted with the purpose of revealing its phase heterogeneity. Analysis of asymmetry of the  $\alpha$ -quartz (100) and (101) reflection profiles suggests that all samples consist of  $\alpha$ - and  $\beta$ -quartz. Quantitative phase and micro-structure analysis on the basis of the Rietveld method showed concentration variations for  $\alpha$ -quartz in the range 65-95 wt.% and 5-35 wt.% for  $\beta$ -quartz. The FullProf and MAUD programs (Rodriguez-Carvajal 2000; Lutterotti 2006) were used for the analysis. Maximum concentration of  $\beta$ -quartz is determined in quartz meta-sandstone of greenschist facies. The average crystallite size <D> for  $\alpha$ -quartz is 60 nm, for  $\beta$ -quartz 15 nm.

Strength properties of the composite binders made on the basis of quartz raw materials are in direct relation to the concentration of  $\beta$ -quartz.

The investigation of changes in phase composition of quartz during mechanic activation desintegration in vibration mill showed monotonous increase of  $\beta$ -quartz concentration against activation time.

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# Fe-Ti oxides in the Tertiary volcanic rocks from the Lower Silesia (SW Poland)

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The Tertiary silica undersaturated, alkaline rocks occur in the area of Lower Silesia forming eastern ending of the Central European Volcanic Province. Basanites, nephelinites, alkali basalts dominate; others lithological types are less common. Major minerals in these rocks are: clinopyroxenes, plagioclases, olivines, nephelines, and Fe-Ti oxides.

Were obtained ca. 500 analyses of chemical composition of Fe-Ti oxides using SEM-EDS method. The main Fe-Ti oxide is Ti-magnetite, which is presents in all studied samples. Ilmenite occurs occasionally forming exolutions in Ti-magnetites. Exolutions of ilmenite in Ti-Fe spinels are common in igneous rocks.

Two types of exolutions were noted in the studied rocks. One of them is "sandwich" exolution, were lamellae of ilmenite are interleaved between lamellae of Ti-magnetite. In the second type lamellae of ilmenite are formed at the external edges of Ti-magnetite grains. Both of those types of exolutions can be caused by oxidation of ulvöspinel component in Ti-magnetites in time of magma cooling. The second type can originate during simultaneous crystallization of ilmenite and Fe-Ti spinel.

Specific distribution of Cr can be observed in analysed samples. In the Ti-magnetite lamellae content of Cr is much higher (ca. 0.6 wt.%  $Cr_2O_3$ ) than in ilmenite (usually below the detection limit). This relationship can be connected with segregation of Cr in exchange reaction during exolution.

Clinopyroxene or olivine inclusions occur often in Ti-magnetite crystals or in two-phase Ti-magnetite and ilmenite grains. The opposite situation can also be found i.e. Ti-magnetite inclusions in clinopyroxene or olivine phenocrysts. During fractional crystallization, when the activity of oxygen is at the constant level, simultaneous crystallization of Fe-Ti oxides with olivine and next Fe-Ti oxides with pyroxene is possible.

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## Evolution of physical processes in an actively deforming magma chamber: the Jizera granite, Bohemian Massif

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In the porphyritic Jizera granite, Bohemian Massif, magmatic fabrics and mafic schlieren were examined in an underground tunnel at depth of up to 140 m below the surface. Computer-based image analysis of K-feldspar phenocrysts (traced from photographs) along 200 m long section of the tunnel revealed complex variations in fabric orientation and intensity, where domains of homogeneous fabric alternate with random phenocryst alignment at the scale of meters to tens of meters. Phenocrysts also follow a "wave-like" trajectories with a meter-scale wavelength in some places. This large-scale K-feldspar fabric pattern is cross-cut by variously-shaped meter-scale channels delineated by biotite schlieren. These structures presumably formed during laminar magma flow along channel-like domains, localized within the high-strength framework of interlocked phenocrysts. After the cessation or deceleration of channel flow, gravity-driven processes operated within the flow channels.

The above interpretations were corroborated by the electron backscatter diffraction (EBSD) method, which indicates multiple but distinct lattice-preferred orientations of biotite grains in the schlieren-bearing magmatic structures, interpreted as reflecting velocity-gradient laminar flow and grain-scale gravity-driven movements of non-Newtonian magma. The complexity in the K-feldspar phenocryst fabric and schlierenbearing magmatic structures contrasts with homogeneous orientation of magnetic fabric of the host granite (carried by coaxial contribution of magnetite, maghemite, and biotite), as revealed by the anisotropy of magnetic susceptibility method (AMS). Magnetic foliations are steep and strike ~NW-SE, magnetic lineations are subhorizontal and trend ~NW-SE along the entire examined section of the tunnel.

We interpret that the above data record the following evolution of physical processes in the Jizera granite magma chamber at multiple scales. Chamber-scale magma mixing and hybridization, as suggested by recent petrologic studies, was replaced by complex laminar flow of highly viscous phenocryst mush (recorded by the K-feldspar fabric). After lockingup of the phenocryst framework, magma flow became highly localized to the meter-scale schlieren-delineated channels. Finally, differential (tectonic?) stresses were transmitted across this highly solidified portion of the magma chamber, resulting in the homogeneous reorientation of magnetite and biotite grains in the interstitial melt pockets and films, as recorded by AMS of the host granite.

# Field trips

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Pre-Conference field trip – Thursday, September 11, 2008

A1.

# Strzegom-Sobótka massif (Sudetes, SW Poland) - an example of a complex late-Variscan granitic intrusion and its pegmatitic mineralization

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**Abstract:** Since the XIX<sup>th</sup> century the Strzegom-Sobótka granitic massif is regarded as one of the classical occurrences of intragranitic miarolitic and vein pegmatites famous for their complex hydrothermal mineral assemblages. The tour is intended to present the participants with the recent state of knowledge on various aspects of magmatic and postmagmatic evolution of these pegmatites and the host granites. Mineralogical *clou* of the trip are visits to working quarries providing the unique opportunity of collecting fresh samples.

**Key-words:** REE pegmatites, miarolitic pegmatites, geochronology, magma evolution, hydrothermal alterations, granite, Strzegom-Sobótka, Sudetes

### Introduction

The Strzegom-Sobótka massif is a large centre of granite mining with well over 60 active quarries producing most of granitic and feldspar raw material mined in Poland. It is situated in the central part of the Fore-Sudetic Block forming an about 50 km long and up to ca. 20 km wide NW-SE elongated zone (Fig. 1).

The massif is a composite intrusion divided into two distinct parts separated by a regional fault (Majerowicz, 1972; Puziewicz 1990). The western part is composed mainly of hornblende–biotite monzogranite (see point 2) with subordinate biotite monzogranite while biotite granodiorite and two-mica monzogranite build the eastern part together with minor bodies of tonalite and alaskite. Following the Barbarin's classification of granitoids, the monzogranites of the western part belong to K-rich calc-alkaline series, the biotite granodiorite is an amphibole-rich calc-alkaline granitoid and the two-mica monzogranite should be classified as a muscovite-bearing peraluminous granitoid.

Igneous activity in this area occurred in the Upper Carboniferous-Lower Permian. Most of the granitic bodies and associated pneumatolitic/hydrothermal mineralization formed at ca. 310–294Ma (Turniak et al. 2005; Mikulski & Stein, 2007). The older age of 324±7Ma
(Rb-Sr method on biotite) was reported only for the two-mica monzogranite (Pin et al. 1989) and is put in question by recently obtained geochronological data (see point 3).

The two parts of the massif differ in the amount and character of postmagmatic products as aplites, aplogranites and pegmatites. The western part shows features of a shallow level intrusion and abounds in miarolitic pegmatites, zoned pegmatitic veins, pegmatitic pods and schlieren as well as aplites. Among mineralogists and mineral collectors the Strzegom-Sobótka massif is renowned for the wealth of well-developed crystals yielded by the miarolitic pegmatites (see point 2). Relatively primitive pegmatitic pods and veins and scarce aplites occur in the eastern part (see point 3).

This composite character of the pluton is explained by multiple intrusions of two (Kural & Morawski 1968; Majerowicz 1972) or four different magma batches (Puziewicz 1985 fide Puziewicz 1990; Pin et al. 1989) that produced a suite of various rock facies. Evolution of the granitic magma in the western part of the massif was governed by fractional crystallization coupled by mixing with small portions of more basic magma (Domańska-Siuda 2007).



Fig. 1. Simplified geological map of the Strzegom-Sobótka massif (*after* Majerowicz 1972; Pin *et al.* 1989). *inlet*: 1 – Kaczawa complex, 2 – Roztoka-Mokrzeszów trough, 3 – Góry Sowie massif, 4 – Ślęża ophiolite, 5 – low-grade metamorphic rocks, 6 – Strzegom-Sobótka massif.

Hydrothermal alterations of the Strzegom-Sobótka granites were simultaneous with the last stage of their formation. Hot, mineralized fluids penetrated the rocks destabilizing local thermodynamic equilibrium, altering the primary magmatic minerals and depositing primary hydrothermal phases (see point 1).

#### Stop 1. Borów 17 quarry

The hornblende-biotite monzogranite and accompanying pegmatites in Borów are described in details at stop 2. However the quarry offers also a possibility to observe

intensive hydrothermal alterations of the rock (Ciesielczuk 2000a, 2000b). A representative 80 m brittle shear zone is exposed in the northern wall, which is cut by many veins with hydrothermal minerals. The shear zone of similar direction crops out also in the nearby "Lubelski" quarry. The altered granite may be divided into a suite of macroscopically distinct types with varying mineral composition (Fig. 2). Also their chemical composition changes with increasing influence of hydrothermal fluids.

The SiO<sub>2</sub> and Na<sub>2</sub>O contents decrease whereas  $Al_2O_3$  and  $K_2O$  rise. Calcium was removed from the altered granite due to plagioclase decomposition. Although no hydrothermal Ca-mineral crystallized, traces of calcium are held in small but frequent apatite grains. Iron, released mainly from biotite, is present in chlorites and pyrites. Trace elements as Cr, Nb, V, La, Rb, Nd, Y were relatively immobile during the hydrothermal alteration. However the amount of Ba, S and Cu increased while Zn, Pb and Sr decreased. The rock volume generally decreases with progressive alteration (Ciesielczuk 2000b; Fig. 2).

There is no apparent relation between the hydrothermal assemblages present within the shear zone described and the pegmatites, which are exposed in this quarry.

#### Stop 2. Strzegom-Żółkiewka, "Andrzej" quarry

The active "Andrzej" quarry at Żółkiewka (Pilgrimshain) exposes hornblende-biotite monzogranite, the predominant rock type of the Strzegom-Sobótka massif. The light grey, equigranular, medium to coarse-grained rock with non-directional fabric exhibits locally porphyritic texture with large alkali feldspar phenocrystals. It consists of perthitic microcline, zonal plagioclase (rim  $An_{0.27}$ ; core  $An_{9.48}$ ), quartz, hornblende (ferrohornblende and ferrohornblende-tschermakite) and dark mica (siderophyllite-annite). Zircon, apatite, allanite, sphene, rutile, monazite, xenotime and opaque minerals are accessory phases. The granite contains many mafic microgranular enclaves (MME) and xenoliths. Comparing to the host granite the MMEs differ in mineral proportions and show the composition of diorite, quartz-diorite, tonalite and granodiorite. Scarce plagioclase and/or alkali feldspar phenocrysts have been mechanically introduced into the enclave. Locally the enclaves show chilled margins and in the marginal parts their components grew outward into the granite.

On the other hand the granite constituents present a typical "inward" growth morphology. All the MMEs show magmatic textures and hybridization signature is common. The main process responsible for enclaves evolution was their contamination by granitic melt at the early stage of granitic magma evolution (Domańska-Siuda 2007). The country-rocks xenoliths, mainly hornfelses and schists, are dark, fine-grained rocks with metamorphic textures. Size of the xenoliths varies ranging typically between 5 and 20 cm in length. They have irregular shape and display sharp contacts with the host granite.

The granite of this area shows features typical for shallow-level intrusion of water-rich magma: abundant miarolitic pegmatites, pegmatitic veins and pods, aplites, numerous schlieren of dark minerals, load structures and local convection chambers (Janeczek 1985; Puziewicz 1990). The rock also varies in grain size and the amount of dark components.

The first written records about regular granite mining activity near Strzegom dates back to 1689. The mining industry flourished particularly in the 19<sup>th</sup> century when a number of quarries (still active) were set in the area. It evoked the common interest in local minerals retrieved for many public and private collections. Many localities as e.g. Grabina, Pielgrzymka, Strzegom, Wzgórze Wiatraczne and Lisie Wzgórze (German names: Graben, Pilgrimshain, Striegau, Windmühlenberg and Fuchsberge) became famous as typical examples of mineral crystallization in granitic miarolitic pegmatites. In 1924 Kalb gave the name *Striegau* to a pseudotetragonal habit of some microcline crystals dominated by (110)

and (101) faces with well-developed (010), (001) and (201) faces. In 1868 Websky, on the other hand, used a Latin version – *Strigovia* to name a certain Fe-rich chlorite variety (*strigovite*), discredited later as a valid species (Janeczek 1985). About 80 mineral species have been recognised in the Strzegom pegmatites so far (Tab. 1).

plagioclase microcline quartz	XXX XX XXX	XXX XXX	XXX XXX	XXX XXX	XXX X	XXX XXX	XXX XX	XXX XXX	XX
biotite	X								
albite		XXX	XX	XX	XXX	XXX	XXX		XXX
post-biotite chlorite	X	X	X		X	X	X		X
spherolitic chlorite		X	X	X	X	X	XX		X
muscovite			X					XX	
pyrite		X	Х	X		X	X		



Fig. 2. Progressive hydrothermal alteration of hornblende-biotite monzogranite in Borów 17 quarry (sample 843 on the left). Changes in mineral composition and rock volume are shown. Crosses indicate the amount of the mineral in the sample: XXX – more than 25%, XX – 25-10%, X – 9-1%, x – less than 1%.

The miarolitic cavities occur either isolated in the granite mass or are associated with networked aplogranites. The first are often of a semi-spherical shape with the flat bottom and may reach the size of a few meters, though usually their dimensions range between a few to less than 50 cm. The cavities are surrounded by successive zones of euhedral crystals, graphic quartz-feldspar intergrowths and aplitic envelope. The zone of euhedral crystals may be replaced by blocky K-feldspar with smoky quartz core. The networked miarolitic pegmatites contain closely-spaced cavities whose dimensions rarely exceed 1 cm.

Initial stages of pegmatitic formation were dominated by crystallization of quartz, microcline, albite, oligoclase, biotite and muscovite with many accessory phases, e.g. beryl, garnet, gadolinite, zircon, monazite, xenotime, REE oxides etc.

Sobótka massif (compiled from the literature). native elements calcite genthelvite-helvite bismuth greenalite siderite (Ce)-synchisite grunerite: Mn-rich sulphides & sulphosalts malachite heulandite bismuthinite phosphates hornblende: Mn-rich chalcocite hastingsite apatite chalcopyrite monazite laumontite cosalite xenotime microcline covellite tungstates & molybdates milarite enargite wolframite minnesotaite galenite scheelite montmorillonite marcasite wulfenite (in press) muscovite molybdenite silicates nontronite pyrite albite oligoclase: pyrrhotite (Ce)-allanite pseudomorphose sphalerite apophyllite: s of albite vallerite pseudomorphoses of phenakite oxides & calcite/siderite+fluorite prehnite hydroxides babingtonite (Fe<sup>2+</sup>)-pumpellyite cassiterite bavenite quartz scherlite-dravite cryptomelane beryl (including (Y)-fergusonite exceptionally rare heliodor scolecite (Y)-formanite and aquamarine) spessartitebiotite: lepidomelane (Y)-tantalaeschynite almandine goethite celadonite stilbite hematite chabazite thorite thortveitite magnetite chamosite: Fe-rich uraninite chrysocolla titanite halides cordierite topaz epidote-clinozoisite zinnwaldite fluorite favalite: Mn-rich (Ce, La)-fluocerite zircon carbonates ferroaxinite (Ce)-bastnäsite

Tab. 1. List of minerals identified in the pegmatites of the western part of the Strzegom-

bismutite

(Y)-gadolinite

The richest assemblage is related to the hydrothermal stage with two different paragenesis: Ca-rich and alkali-Fe-rich (Janeczek 1985; Janeczek 2007). They are antagonistic and remain separated spatially even when present within a single cavity. The first is characterized by epidote, Fe-chlorites, axinite, bavenite and fluorite (combination of {111} and {110} forms) +/- laumontite while cleavlandite, stilpnomelane, milarite, tourmaline, zinnwaldite and fluorite (mainly {111} form) are diagnostic for the latter. Their mineralogical composition became unified in low-temperature with the crystallization of zeolites. The cavity may be partially or completely filled by carbonates or clay minerals.

Epigenetic assemblage comprise such minerals as malachite, chrysocolla, goethite, covellite and cryptomelane.



Fig. 3. About 2.5 cm long crystals of sceptre quartz from Siedlimowice (after Michalik, 1997).

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MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Pre-Conference field trip – Thursday, September 11, 2008

A2.

#### Inverted metamorphic zonation, contact metamorphism and ore deposits in the E-envelope of the Karkonosze granite; the Intra-Sudetic Fault Zone

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**Abstract**: Thrust units and metamorphic zonation of the E-envelope of the Karkonosze Granite: MP/MT Izera-Kowary Unit (orthogneisses, mica schists); HP/HT S-Karkonosze (blueschists) and Leszczyniec (bimodal igneous complex) units. WP and MOR palaeotectonic settings. Blueschist facies metamorphism and greenschist-facies overprint. Tectonic suture and regional context within the Bohemian Massif. Contact metamorphism, mineralization and ore deposits. The Intra-Sudetic Fault Zone = contact between the Karkonosze-Izera Massif and the Kaczawa Unit. Geotourism.

**Key-words:** bimodal meta-igneous, geotectonic settings, blueschist facies, contact metamorphism, Variscan thrusting, ore deposits, Karkonosze-Izera Massif, Intra-Sudetic Fault Zone, geotourism

#### The Karkonosze-Izera Massif (Ryszard Kryza)

The Karkonosze-Izera-Massif (Fig. A 2-1) comprises the Variscan Karkonosze granite and its Neoproterozoic-Palaeozoic metamorphic envelope.

Several lithostratigraphic and tectonic subdivisions have been proposed for the metamorphic series of the IKB (see overview in Oberc-Dziedzic *et al.*, in print). In the tectonic scheme developed by several authors (Mazur 1995, Kryza & Mazur 1995, Mazur & Kryza 1996, Mazur and Aleksandrowski 2001), and recently modified by Oberc-Dziedzic *et al.* (in print; Fig. A 2-2), the metamorphic envelope of the Karkonosze granite is interpreted as a pile of four thrust units showing different lithostratigraphy and metamorphic evolution (from bottom to top): (1) the Izera-Kowary, (2) Ještěd, (3) South Karkonosze, and (4) Leszczyniec units.

The granitic protoliths of the Izera gneisses were dated by various methods at 515-480 Ma (see overview in Oberc-Dziedzic *et al.*, in print). The Kowary and Karkonosze gneisses have similar ages of around 492 - 481 Ma (U-Pb ages, Oliver *et al.* 1993), and of  $501.5\pm1.1$  - Ma  $503.2\pm1$  Ma ( $^{207}$ Pb/ $^{206}$ Pb mean ages, Kröner *et al.* 2001), respectively. The Izera and Kowary gneisses are accompanied by the ca. 1000 m thick schist series of the Velká Úpa Group (Fig. A2-1).

The Izera-Kowary Unit experienced progressive MP-MT metamorphism, up to the low amphibolite facies conditions, locally overprinted by contact metamorphism caused by the Karkonosze intrusion (Kryza & Mazur 1995).



Fig. A 2-1. Geological sketch map of the Karkonosze-Izera Massif (Oberc-Dziedzic *et al.* in press). KIM – Karkonosze-Izera Massif. Inset map: EFZ – Elbe Fault Zone, ISF – Intra-Sudetic Fault, MGH – Mid-German High, MO – Moldanubian Zone, MS – Moravo-Silesian Zone, NP – Northern Phyllite Zone, OFZ – Odra Fault Zone, RH – Rhenohercynian Zone, SBF – Sudetic Boundary Fault, SX – Saxothuringian Zone, TB – Teplá-Barrandian Zone. Rectangle shows the position of KIM in the Bohemian Massif.

The Ještěd Unit is a small fault-bounded element exposed at the SW edge of KIM. It is composed of Middle - Upper Devonian and Lower Carboniferous metasedimentary rocks subjected only to very weak, medium-pressure metamorphism (Mazur *et al.* 2006, and refs therein).

To the south and east, the Izera-Kowary Unit plunges below the South Karkonosze and the Leszczyniec units (Fig. A 2-1). The South Karkonosze Unit is formed of a several hundred metres thick sequence of Ordovician to Devonian(?) metasedimentary rocks (Chlupáč 1997), with minor intercalations of greenstone and diabase. The upper part of the sequence, stretching along the southern margin of KIM, comprises metavolcanic rocks, including basic lavas and volcaniclastics of P-MORB affinities, and felsic rocks of within-plate geochemical signature (Patočka & Hladil 1998). The lowermost Ordovician basic metavolcanic rocks (dated by <sup>87</sup>Rb-<sup>86</sup>Sr method; Bendl *et al.* 1997) preserve records of early

blueschist facies metamorphism (Kryza & Mazur 1995 and refs therein) of around 360 Ma, followed by greenschist overprint at ca. 340 Ma (<sup>40</sup>Ar-<sup>39</sup>Ar ages; Maluski & Patočka 1997).





The Leszczyniec Unit in the eastern part of KIM is an Early Ordovician (U-Pb zircon ages 494±2 Ma, Oliver *et al.* 1993, and ca. 490 Ma, Bachliński & Smulikowski 2005) metaigneous complex composed of fine-grained schistose and medium-grained massive metabasites, felsic gneisses and metadiorites. The rocks of the Leszczyniec Unit show geochemical characteristics of N-MORB (Kryza *et al.* 1995, Winchester *et al.* 1995), except for the metadiorites that are similar to island-arc (Narębski 1980) or crustally-contaminated rift-related magmas. The rocks of the Leszczyniec Unit might have been

emplaced in an extensional rift setting, although the observed large proportion of felsic rocks seems to preclude a mature oceanic rift (Kryza *et al.* 1995). The rocks experienced relatively HP and MT metamorphism (Kryza & Mazur 1995).



Fig. A 2-3. Simplified P-T metamorphic paths for the tectonic units of the eastern cover of the Karkonosze pluton. The shaded rectangle represents the P-T field of the contact metamorphism. PK – South Karkonosze Unit, L – Leszczyniec Unit, K – Izera-Kowary Unit (after Kryza & Mazur 1995).

The four structural units described have been interpreted as elements of the nappe structure of KIM (Mazur 1995, Mazur & Kryza 1996, Mazur & Aleksandrowski 2001, but see also other interpretations by Seston et al. 2000 and Kozdrój et al. 2001). According to Mazur and Aleksandrowski (2001), the Izera-Kowary Unit, together with the Lusatian Massif adjacent to the NW (Figs. A 2-1 and 2), represent the pre-Variscan continental basement of the Saxothuringian basin. The very low-grade metamorphic rocks of the Ješted Unit correspond to the sedimentary infill of this basin. The Ješted Unit is tectonically sandwiched between the underlying basement rocks of the Izera-Kowary Unit and the overlying South Karkonosze Unit. The South Karkonosze Unit is, apparently, composed of a number of smaller thrust sheets or slices, showing mutually similar structural and metamorphic histories (Mazur 1995, Kryza & Mazur 1995). The two uppermost units (South Karkonosze and Leszczyniec units) show evidence of, respectively, high and moderately high P/T metamorphism (Fig. A 2-3), thus being evidence of overthrust and inverted metamorphic zonation (Kryza & Mazur 1995). The blueschist facies rocks, together with the MOR-type metaigneous rocks in the upper units may delineate a major suture after the closure of an oceanic domain between the Saxothuringian and Tepla-Barrandian crustal blocks (Seston et al. 2000, Aleksandrowski & Mazur 2002, Oberc-Dziedzic et al., in press).

The nappe pile is intruded by the Karkonosze granite pluton. The granite was emplaced shortly after magma generation, probably during the extensional collapse, that corresponds to the final phase of the  $D_2$  deformation in West Sudetes Mazur (1995). The petrogenesis and source of the granite has been subject to controversies but based on isotope investigations, Duthou *et al.* (1991) assumed a fairly primitive crustal source for granitic melt. Słaby and Martin (2008) recognized that Kakonosze granite differentiation proceeded through two distinct mechanisms: felsic and mafic magma mixing and fractional crystallization.

The Karkonosze granite was dated by Rb-Sr whole rock isochrone method at  $328\pm12$  Ma ("central" porphyritic granite) and  $309\pm3$  Ma ("ridge" equigranular granite; Duthou *et al.* 1991); Pb/Pb and U/Pb zircon dating yielded diversified ages of  $304\pm14$  Ma for porphyric monzogranite (Kröner *et al.* 1994), and  $314\pm3.3$  Ma and  $318.5\pm3.7$  Ma for porphyritic granites of the NE part of the pluton (Machowiak & Armstrong 2007). New SHRIMP data (T.Oberc-Dziedzic, R.Kryza & C.Pin, 2008, unpublished) indicate that the main porphyritic facies is somewhat older than 320 Ma.

#### Nature protection and geotourism: basic notes (based on Gawlikowska 2000)

#### Karkonosze National Park (KPN)

(established 1959, area 5 573 ha)

The park is located in the top section of the Karkonosze Mts, with two enclaves: Chojnik and Szklarka Waterfall, and it adjoins, along the state border, the Czech Krkonossky narodni park. Since 1992, both parks form a World Biosphere Reserve. The KPN is one of the most attractive tourist regions in Poland. Numerous uncommon postglacial landscape forms: Kocioł Mały (Small Hollow), Wielki Staw (Great Pond), Śnieżne Kotły (Snowy Hollows), the majestic uplift of Śnieżka (1603 m a.s.l.), picturesque granite weathering forms and waterfalls (Kamieńczyk and Szklarka). The area is built mainly of the Variscan Karkonosze granite, being occasionally exploited in two quarries.

#### Rudawy Landscape Park (RPK)

(established 1989, area 15 705 ha)

The park covers the Rudawy Janowickie and adjoining area. The western part is composed of the Variscan Karkonosze granite and its metamorphic envelope, in the east we find Lower Carboniferous sediments of the Intra-Sudetic Basin. In the contact aureole of the Karkonosze granite, metal and other minberal deposits were exploited in several localities, since the middle ages (e.g. Miedzianka, Kowary, Wieściszowice). Two twin cone peaks, Krzyżna Góra (654m) and Sokolik (623m) are the famous landmarks. The main values of the park include the diversity of its geology, remnants of old mining, rock outcrops, weathering forms, landscape, dense forest, and ... fish ponds.

#### Landscape Park of the Bóbr Valley (PKDB)

(established 1989, area 13 270 ha)

The park comprises the Bóbr River valley, 42 km long, between Jelenia Góra and Lwówek Śląski, and the neighbour areas. The river forms picturesque gorges cut mostly in the Izera granite-gneisses. To the north, these rocks are in tectonic contact, along the major Intra-Sudetic Fault Zone, with the low-grade metamorphic Kaczawa Complex. Further north, the river cuts the sedimentary Mesozoic infill of the North- Sudetic Depression. The valley is mostly forested, and offers attractive tourist routes.

#### Stop A 2/1: Kowary – Old Iron-Uranium Mine Location: Kowary town, 17 km SE of Jelenia Góra Geology: the Karkonosze granite and its metamorphic envelope, ore mineralization in the metamorphic cover Leader: Ryszard Kryza

Mining tradition in the vicinity of Kowary town dates back to the XII century when the region began to be explored by the Valonians. Up to the XX century, the main interest of mining was magnetite-haematite iron ore, but around 1920, attention was turned also to uranium mineralization. After the World War II, Kowary became a "top-secret" uranium mine, strictly controlled by Soviet military administration. Until 1973, when the mine was closed, 24 adits had been made, with a total length of 74 km, and down to a depth of 525 m. In 1974-1989 a radon "inhalation plant" operated there, associated with Cieplice Spa. In 2000, a Tourist Underground Path was opened, and in 2002, the "inhalation plant" was reopened again.

The iron-uranium ore deposit of Kowary is located within mica schists and gneisses of the metamorphic envelope of the Karkonosze granite. The deposit is a bent-lens in shape, ca. 1500 m long and up to 200 m wide. The ore bodies are developed within horfelses, amphibolites and scarns, near the contact with the Karkonosze granite that is faulted and cut by aplite and pegmatite veins.

The deposit comprises three types of ore-mineral assemblages:

1. magnetite ore: magnetite, maghemite, minor ilmenite, pyrite, and rare pyrrhotite and arsenopyrite;

2. sulphide ore: pyrrhotite-pyrite, with chalcopyrite, marcasite, and rare sphalerite and galena;

3. polymetalic ore: chloantite, safflorite, rammelsbergite, and minor nickeline, native arsenic, native bismuth, native silver and uranium minerals.

Ores (1) and (2) are found as veins and nest-aggregates within (1) and within surrounding rocks. The uranium mineralization is bound to the polymetalic ore and it forms three associations:

- (a) uranium black aresnopyrite chalcopyrite coffinite,
- (b) uranium black schapbachite chalcopyrite nickeline,
- (c) uranium black clausthalite coffinite or uranium black tiemannite chalcopyrite cinnabar.

Particularly rich U-mineralization was observed in strongly tectonised zones, along contacts of various lithologies and near faults where uranium black was found in calcite-and calcite-barite veins and in breccias.

The iron-uranium mineralization is classified as a metamorphic/contact-metasomatic deposit.

(Source used: Muzeum Minerałów, Towarzystwo Geologiczne Spirifer, Nowa Ruda, http://www.redbor.pl/index.html, "Górnictwo uranu w Polsce").

#### Stop A 2/2: Kowary Pass – Kowary gneisses

Location: 2.5 km SE of Kowary, ca. 1.5 km N of Kowary Pass Geology: the Kowary gneisses of the Izera-Kowary Unit Leader: Ryszard Kryza

The Kowary gneisses represent early Ordovician (ca. 500 Ma) granite intrusion deformed and metamorphosed under greenschist facies conditions during the Variscan

orogeny (Kryza & Mazur 1995). Together with mica schists, they belong to the Izera-Kowary Unit, which is the lowermost tectonic unit of the eastern metamorphic cover of the Karkonosze granite (Mazur 1995, Oberc-Dziedzic *et al.*, in press).

The Kowary gneisses are coarse-grained rocks showing a sequence of textural varieties depending on the degree of deformation, and displaying mutual transitions: porphyritic, coarse-grained granite – augen gneiss – flaser gneiss – layered gneiss. Fine-layered Kowary gneisses form narrow zones at the contact with mica schists. All varieties of the gneisses contain variably deformed K-feldspar megacrysts, more or less intensely replaced by chessboard albite. The matrix is composed of albite, quartz, biotite often accompanied by chlorite, white mica, epidote, and accessory apatite and zircon. The gneisses are calcalkaline and peraluminous in character; the high  $P_2O_5$  content in the orthogneiss is typical of the S-type granites (Oberc-Dziedzic *et al.*, in press). The ortogneisses are intruded by thin mafic dykes altered into biotite-amphibole schists.

The foliation in the gneisses dips at 65-80° to SE, and the mineral lineation (elongated feldspar megacrysts and aligned mineral aggregates) broadly follows the foliation dip. The fabric was develop during normal faulting corresponding to extentional collapse (top to SE) (Mazur 1995).

Recent SHRIMP dating of zircons (Oberc-Dziedzic *et al.*, in press) shows that the main population of zircons is dispersed within a range of ca. 470–500 Ma, with an average Concordia age of ca. 490 Ma. This is in a good agreement with the well established Early Ordovician magmatism in this area and with the earlier U-Pb zircon dating of the Kowary gneisses (Oliver et al.1993, Kröner et al. 2001). Similar ages obtained for the neighbouring quartzo-feldspathic rocks in the mica schists imply that the schists, at least locally, do not represent the original country rocks for the orthogneiss protolith intrusion, and that the contact between them are tectonic (Oberc-Dziedzic *et al.*, in press).

#### Stop A 2/3: Ogorzelec – Paczyn gneisses and metabasites of the Leszczyniec Unit Location: Ogorzelec quarry, 6 km SE of Kowary Geology: the Paczyn gneisses and the Leszczyniec Unit metabasites Leader: Ryszard Kryza

The Ogorzelec quarry exposes intrusive relationships of the felsic Paczyn gneisses against their metabasic country rocks (amphibolites), all belonging to the Leszczyniec Metaigneous Complex (or Leszczyniec Unit). These rocks were dated by U-Pb method on zircons at ca. 490-500 Ma (Oliver *et al.* 1993, Bachliński & Smulikowski 2005).

The main body of the felsic gneisses, a few tens of metres large, is rather weakly deformed compared to the surrounding amphibolites. The gneiss branches away from the main body, forming a few smaller apophyses within the amphibolites. The gneisses are composed of quartz, albite (An 0.2-6.3) and epidote, accompanied by very minor mafic minerals (chlorite, phengite, actinolite and stilpnomelane). The protolith of the gneisses should correspond to leucocratic tonalites or trondhjemites (Narębski *et al.* 1986, Kryza *et al.* 1995).

The amphibolites are composed of albite (An 0.2-8.5) and magnesiohornblende, the association typical of epidote-amphibolite facies. Hornblende crystals are cored by actinolite and reveal evidence for the progressive metamorpism (Kryza & Mazur 1995). The amphibolites bear NNE-SSW lineation developed on sub-vertical or steep, ESE-dipping foliation (Mazur 1995).

The bimodal suite of metaigneous rocks in the Ogorzelec quarry is representative of the Leszczyniec Unit. The mafic rocks show N-MORB affinieties, whereas the felsic varieties

represent their fractionation-related counterparts, partly contaminated by continental crustal materials (Kryza *et al.* 1995, Winchester *et al.* 1995).

The metamorphism in the Leszczyniec Unit is relatively high P/T and corresponds to the epidote-amphibolite facies. The P/T gradient seems to be lower and the metamorphic grade slightly higher compared with the HP/LT South Karkonosze Unit southwards (Kryza & Mazur 1995; see Fig. A 2-3), however, the two structurally upper external units are interpreted to delineate a major tectonic suture along the eastern egde of the Karkonosze-Izera Massif (Seston *et al.* 2000, Aleksandrowski & Mazur 2002).

# Stop A 2/4: Pilchowice – The Intra-Sudetic Fault Zone: contact between the Karkonosze-Izera Massif and the Kaczawa Metamorphic Unit Location: the Bóbr valley S of Pilchowice, 10 km NW of Jelenia Góra Geology: the Izera gneisses, the Kaczawa low-grade metamorphic rocks, the Intra-Sudetic Fault Zone

#### Leader: Ryszard Kryza (partly based on Aleksandrowski et al. 1997)

One of the most important tectonic boundaries in the West Sudetes, the Intra-Sudetic Fault Zone, is exposed along a ca. 500 m long profile along the Bóbr river valley at Pilchowice. The outcrop pattern is complicated by a map-scale strike-slip duplex structure (Alexandrowski *et al.* 1997; Fig. A 2-4).



Fig. A 2-4. Geology of Pilchowice interpreted in terms of sinistral strike-slip duplex at the transition zone between the Kaczawa and Izera metamorphic units (based on unpubl. data of Baranowski 1967, Geol. Map of the Sudetes 1 : 25 000, and Aleksandrowski *et al.* 1997).

Along the profile on the west bank of the river, ca. 500 m west of the dam, from south to north we observe: (a) the Izera granites and granite-gneisses, (b) steep fault zone dominated by strongly deformed gneisses and mylonites developed at the expense of the Kaczawa phyllites, (c) phyllites of the Kaczawa Complex.

The variously deformed Izera gneisses have developed from the ca. 500 Ma Izera granites (Oliver *et al.* 1993). They are composed of quartz (locally bluish), K-feldspar and plagioclase, minor white mica and chlorite (partly after biotite). The observed inverted zonation in plagioclase (< 1 % An in core and ca. 8 % An in rim) suggests progressive metamorphism under the greenschist facies conditions.

The 1-2 metre thick mylonite at the very contact between the Izera gneisses and the Kaczawa phyllites has developed at the cost of the latter which is evident from the very heterogeneous zircon populations within the mylonite, typical of metasedimentary rocks. The metasedimentary rocks of the Kaczawa Complex further north are significantly less recrystallized (slates) and display relics of sedimentary structures (detrital grains, lamination and graded bedding).

A detailed structural study (Aleksandrowski *et al.* 1997) showed that in both metamorphic complexes the main foliation strikes WNW-ESE and dips steeply to NNE. The foliation displays stretching lineation which plunges to WNW or ESE at shallow angles. The rocks show a range of kinematic indicators developed in ductile and semi-brittle to brittle conditions (asymmetric pressure shadows, winged feldspars, mica fishes, quartz *c*-axes patterns, shear bands, bookshelf sliding of fractured prophyroclasts etc.) which point to both sinistral (at both ductile and brittle conditions) and dextral (at ductile to semi-brittle conditions) sense of the shear which occurred in the proximity of the Intra-Sudetic fault zone.

It is difficult to assess the PT metamorphic conditions experienced by the rock exposed on both sides of the fault. The most informative can be the compositional range and zonation of white mica. In the Izera gneiss south of the fault, the Si contents in white mica varies from ca. 3.05-3.10 in cores, to 3.10-3.45 in rims and in tiny flakes in the matrix. Most of the micas in the schists (mylonites) of the fault zone cluster around 3.30 which may indicate that the main stage of the white mica recrystallization (at the presently exposed depth level) occurred at ca. 6 kbar (at assumed T around 400°C). In a slate of the Kaczawa Complex to the north, the Si contents in micas are significantly lower (3.05-3.20), indicating possibly lower minimum pressures (based on Pgh barometry of Massonne & Schreyer 1987; R.Kryza, R.Zagórda and G.Fedorowicz, 1998 unpublished).

The structural interpretation presented here is based on a structural study by Aleksandrowski *et al.* (1997). Effects of three main deformational events have been recorded in both structural units adjacent to the Intra-Sudetic Fault near Pilchowice. The oldest event D<sub>1</sub> (probably Late Devonian to Early Carboniferous in age) resulted in a penetrative, ductile, sinistral shear fabric in the Góry Izerskie gneisses. Its present-day orientation was achieved through later reorientation of originally SE-dipping foliation related to regional, NW-directed thrusting (Mazur 1995; Fig. A 2-5). The reorientation occurred on the northern slope of a domal structure which grew above the Karkonosze granite intrusion during the Visean. This was postdated by an important strike-slip dextral displacement (event D<sub>2</sub> - late Early Carboniferous?) on the Intra-Sudetic Fault, which

produced prominent pervasive *s*-*c* fabric in the Góry Kaczawskie phyllites and ductile to semi-brittle, localised shear zones in the Góry Izerskie gneisses, superimposed on the older, sinistrally oriented fabric. The subsequent sinistral movement of the event D<sub>3</sub> (Late Carboniferous ?) brought about sporadic semi-brittle mesoscopic structures in both gneisses and phyllites as well as a map-scale strike-slip duplex on the Góry Izerskie/Kaczawskie boundary (Aleksandrowski *et al.* 1997).

The Intra-Sudetic fault is believed to represent an important strike-slip terrane boundary at the NE periphery of the Variscan belt, with a possible large dextral displacement (Aleksandrowski *et al.* 1997), juxtaposing the Saxothuringian, Tepla-Barrandian and Moldanubian terranes of Armorican affinities to the south with an oceanic (Rheic) accretionary prism of the Kaczawa complex to the north (Aleksandrowski & Mazur 2002).



Fig. A2-5. Simplified block diagram showing domal shape of the Karkonosze-Izera Massif, acquired during D2 extensional deformation event. The D1 structures, related to NW-thrusting event, were reoriented on slopes of the dome. KG - Karkonosze Granite Massif (Mazur 1995, Mazur & Kryza 1996, Aleksandrowski *et al.* 1997).

Attempts at direct dating of the strike-slip displacements on the Intra-Sudetic fault were made by Oliver & Kelley (1993, vide Aleksandrowski & Mazur 2002), with  $^{40}$ Ar/ $^{39}$ Ar method, yielding ages of 338±15, 312±38, 302±47 and 228±10 Ma for biotite and 299±21 Ma for muscovite from mylonitised Izera gneiss sampled at Pilchowice. They were followed by those of Marheine *et al.* (2002), who, using the same method, arrived at ages of 333±3 and 324±3 Ma for muscovites in two samples of the same rocks. This scatter of ages may reflect relatively long-lasting and multistage displacements on the Intra-Sudetic Fault.

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Post-Conference fiels trip - Sunday, September 14, 2008

B1.

## Variscan lower-crustal HP-HT granulites and migmatitic country rocks of the Góry Sowie Massif. Ślęża Ophiolite: petrology and geotectonic context

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**Abstract:** HP-HT granulites, ultramafites and surrounding migmatites of the Góry Sowie Massif; P-T paths and timing of Variscan metamorphism; Variscan exhumation. The Central-Sudetic ophiolites: petrology, geochemistry, age, palaeotectonic setting, structural and metamorphic evolution; tectonic position of the ophiolites in the Variscan context. Geotourism.

**Key-words:** granulites, ultramafites, migmatites, ophiolites, geochemistry, geochronology, Variscides, geotourism

#### The Góry Sowie Massif (Ryszard Kryza)

The fault-bounded Góry Sowie Massif (GSM) is composed mainly of gneisses and migmatites accompanied by minor mafic and ultramafic rocks and a few small granulite bodies. The most widespread gneisses and migmatites are composed of quartz, plagioclase (An<sub>15-35</sub>), biotite and, locally, garnet, sillimanite, K-feldspar, +/- muscovite, +/- cordierite. The gneissic complex has undergone polymetamorphic evolution (Kryza 1981, Żelaźniewicz 1990). An early metamorphic episode, with relatively high P/T gradient, is inferred from widespread relict kyanite. The older assemblage was overprinted by a high amphibolite facies metamorphism, under a moderate P/T gradient, as indicated by the coexistence of sillimanite, K-feldspar, and garnet. Subsequently, locally intense anatectic melting, obviously controlled by variation in lithology and by fluid distribution, produced diatexites and "*in situ* granites" (Kryza 1981). Żelaźniewicz (1990) inferred five tectonometamorphic events, D<sub>1</sub> - D<sub>5</sub>, in the gneisses. The metamorphic climax and migmatization have been ascribed to the D<sub>2</sub> and D<sub>3</sub> events, and their waning stage is interpreted to have happened 380 -370 Ma ago (van Breemen *et al.* 1988, Bröcker *et al.* 1998, Timmermann *et al.* 2000).

Felsic granulites, with thin intermediate intercalations, occur in several small outcrops in the northern part of the Góry Sowie. These HT and HP granulites host lensoid bodies of strongly serpentinized mantle-derived ultramafic rocks, mostly harzburgites and lherzolites with spinel and pyrope garnet. Sm-Nd Grt-WR-Cpx ages of 403 and 386 Ma were obtained, for cores and rims respectively (Brückner *et al.* 1996). Similar ages of ca. 400 Ma, obtained





Fig. B 1-1. P-T-t paths for the Góry Sowie granulites and host migmatites (after Kryza & Fanning 2007).

The Variscan tectonic movements exhumed the high-grade metamorphic rocks, including the HT-HP granulites, from deep crustal levels (Kryza *et al.* 1996). An early (pre-Upper Devonian) uplift of the Góry Sowie Massif is ascribed by Aleksandrowski *et al.* (2000) to the initial Eo-Variscan convergence. This concept is essentially consistent with numerous geochronological data obtained over the past twenty years in the Góry Sowie Massif. The granulite-facies metamorphism dated at 401.5  $\pm$ 0.9 Ma (O'Brien *et al.* 1997) was soon followed in that area by a rapid decompression to amphibolite facies conditions. The latter temperature dominated metamorphism took place between ca. 400 and 370 Ma (Timmerman *et al.* 2000, Żelaźniewicz 2003, Kryza & Fanning 2007, and refs. therein) and was eventually terminated by the exhumation of the Góry Sowie gneisses. The gneisses must have been at the surface by the end of Devonian since they already supplied detritus to the neighbouring Świebodzice Basin (Porębski 1981). Nevertheless, in the present erosional level, the Góry Sowie gneisses bear also memory of a younger Early Corboniferous thermal

event mostly related to the widespread mylonitization, especially in the adjacent Niemcza Zone (Steltenpohl *et al.* 1993).

Summing up, the critically reviewed geochronological data indicate that we are dealing with the following well recognized thermal events in the Góry Sowie Massif:

- ca. 500 Ma: magmatic crystallization (granites or rather their reworked products as protoliths for the gneisses and migmatites),

- ca. 400 Ma: HT-HP granulite facies metamorphism (in parts of the rock complex),

- ca. 380–370 Ma: amphibolite facies metamorphism and migmatization, and subsequent rapid uplift.

#### Nature protection and geotourism: basic notes (based on Gawlikowska 2000)

#### Góry Sowie Landscape Park (PKGS)

(established 1991, area 8 141 ha)

The PKGS covers the central part of the Sowie Mountains (Góry Sowie) in the central Sudetes, with their highest peak of Wielka Sowa (1015 m a.s.l.). The largely forested area (94 %) has a beautiful landscape, with steep hills, deep valleys and many picturesque crags. The area is part of the Góry Sowie Massif composed of high-grade metamorphic gneisses and migmatites, and intercalations of high-pressure–high-temperature granulites and associated mantle-derived ultramafic rocks. In semi-grabens, Lower Craboniferous molasses-type sediments are preserved, locally associated with late-Variscan subvolcanic/volcanic rocks (kersantites and rhyolites).Special tourist importance has the system of adits and underground chambers worked out by concentration camp prisoners during the World War II and seemingly planned as German military factories.

#### Stop B 1/1: Góry Sowie / Bystrzyca Górna

### Location: Bystrzyca Górna village, 7.5 km SWS of Świdnica, optional: railway cut and/or river bed

Geology: the Góry Sowie Massif, felsic granulites, Grt-meta-peridotites, serpentinites, ca. 400 Ma peak metamorphism age

#### Leaders: Ryszard Kryza, Piotr Gunia

The railway cut exposes felsic granulites associated with serpentinites and other partly altered meta-ultramites. The felsic granulites are fine- to medium-grained rocks, massive-to variously banded rocks composed of quartz, perthitic K-feldspar and plagioclase, garnet, kyanite, rutile and ilmenite; locally abundant biotite is mostly a secondary phase as is white mica. In a nearby exposure, intercalations of intermediate CPx-bearing granulites have been described.

The meta-ultramafites form lansoid inclusions and boudins within the felsic granulites (contacts well exposed in an abandoned quarry ca. 800 m to S, not to be visited). The ultramafics display a large mineralogical variation, from totally serpentinized rocks to weakly altered CPx-Am-Grt-bearing rocks (so called piribolites). Based on relict mineralogy and CIPW norm, spinel and pyrope-bearing harzburgites and lherzolites were the most common protoliths. The P-T conditions for the garnet peridotites were estimated to be 1 300° C and 20–30 kbar for cores of grains and 800° C and 16 kbar for rims (Bakun-Czubarow 1983). Sm-Nd Grt-WR-Cpx ages of 403 and 386 Ma were obtained for cores and rims respectively (Brückner *et al.* 1996).

#### Stop B 1/2: Góry Sowie / Zagórze Śląskie ("Fregata") Location: Road-cut, 11.0 km SWS of Świdnica, S bank of Bystrzyckie Lake Geology: the Góry Sowie Massif, felsic granulites, ca. 400 Ma peak metamorphism age Leader: Ryszard Kryza

Locality "Fregata" at Bystrzyckie Lake in Zagórze is a type locality for the Góry Sowie granulites. The felsic granulites form an aligned body a few hundred meters long and up to tens meters thick within migmatites. The unaltered granulites are pale-grey, pinkish fine- to medium-grained rocks, usually banded, with garnet- and secondary biotite-rich, and quartz + feldspar-rich laminae. Common kyanite is easily discernable, whereas accessory rutile, ilmenite, and obviously secondary muscovite are additional components. The P-T conditions for the peak granulite facies event were calculated at 18–20 kbar and ca. 900° C, with late decompressive re-equilibration over a range of 4–10 kbar as temperatures decreased to 600–700° C (Kryza *et al.* 1996, O'Brien *et al.* 1997). The latter metamorphic event in the granulites probably coincided with the peak of metamorphism and anatexis in the surrounding gneisses. The peak P-T conditions and the U-Pb zircon ages of around 395–400 Ma (O'Brien *et al.* 1997, Kryza & Fanning 2007) correspond well to those from the meta-ultramafites from Bystrzyca Górna. Xenotime from a pegmatite cutting the granulites at "Fregata" was dated at ca. 370-380 Ma (Timmermann *et al.* 2000).

#### Stop B 1/3: Góry Sowie / Walim

#### Location: Entrance to adits at Walim, 18.0 km SW of Świdnica Geology: the Góry Sowie Massif, granites, sillimanite gneisses and migmatites, ca. 390 Ma migmatization (anatectic granite dykes) Leader: Ryszard Kryza

South of the town of Walim, sillimanite-bearing gneisses and migmatites host granite dykes, up to ca. 1 m thick, generally parallel to the main foliation, but locally displaying discordant, intrusive contacts. The granite is a pale grey, medium-grained massive rock composed of quartz, plagioclase, K-feldspar, muscovite and very subordinate biotite, sillimanite, relict kyanite, and accessory zircon and monazite. The granites have been interpreted as products of anatectic migmatization, locally mobilized and intruding the surrounding gneisses (Kryza 1981). In places, they comprise small shearing bands (cm scale) composed of muscovitized fibrolith and quartz. U-Pb isotopic ages of monazite from these granites is ca. 380 Ma (Timmermann *et al.* 2000).

#### Stop B 1/4: Góry Sowie / Potoczek

#### Location: 16.0 km S of Świdnica, crags at road between Rościszów and Walim Geology: the Góry Sowie Massif, migmatites: nebulites (diatexites), ca. 500 Ma magmatic zircon age, ca. 380 – 370 Ma metamorphism Leader: Ryszard Kryza

The migmatites from Potoczek comprise "homophaneous", granite-like rocks corresponding to "nebulites" (diatexites). They are pale grey, medium- to coarse-grained rocks composed of quartz, subidiomorphic plagioclase, biotite and locally rather common garnet. Typically, the rocks contain abundant loaf-shaped or diffused inclusions, centimeters to decimeters in size, embedded within a granite matrix. They convincingly exemplify an *in situ*, "newly-born" granite. Petrographic features prove anatectic origin of these rocks and subsequent rapid uplift (e.g. zoned plagioclase). The nebulites have been

dated by several authors using Rb-Sr and U-Pb methods, yielding controversial ages. The most recent SHRIMP zircon dating shows ca. 500 Ma ages (Kryza & Fanning 2007) whereas the metamorphism have been dated at 370-380 Ma using Rb-Sr method (Bröcker *et al.* 1998).

#### The Ślęża ophiolite (Ryszard Kryza, Alfred Majerowicz, Piotr Gunia)

The Central Sudetic ophiolites are among best preserved and complete ophiolitic suites in the Variscan Belt. The fairly large ultramafic-mafic complexes along the NE, E and S margins of the Góry Sowie Massif were first recognized as ophiolites in the late 1970-ies (Majerowicz 1979) based on general petrographic features, and later reported geochemical data indicated their MORB affinity. More recent geochemical studies revealed some internal complexities of the suites, e.g. significant geochemical contrast between the plutonic and subvolcanic/volcanic members, but overall confirmed their MOR-type characteristics (Pin *et al.* 1988, Majerowicz & Pin 1994, Floyd *et al.* 2002, and refs. therein).

The magmatic emplacement age of the ophiolites was previously determined at ca. 365 Ma using the Sm-Nd isochrone method (Pin *et al.* 1988) but afterward reinterpreted to ca. 420 Ma based on U-Pb multigrain zircon method (Oliver *et al.* 1993). The latest ages of 400 +4/-3 Ma on zircons from rodingites have been interpreted as corresponding to serpentinization processes (Dubińska *et al.* 2004). Similar ages have recently been obtained by SHRIMP method on zircons from subvolcanic rocks of the Ślęża ophiolite (Kryza, 2008 unpublished data). The mafic rocks of the ophiolites are rather weakly and locally deformed and display only partial metamorphic alteration (Abdel Wahed 1999). The provenance of the ophiolitic suites, their age and relationships to other igneous complexes in the Sudetes, as well as their tectonic position are key problems of this part of the Variscan orogen. Mierzejewski (1993) suggested that the Ślęża ophiolite lies on top of a westward overthrust pile of tectonic units.

#### Nature protection and geotourism: basic notes (based on Gawlikowska 2000)

#### Ślęża Landscape Park (ŚPK)

#### (established 1988, area 8 190 ha)

The ŚLP comprises three parts within a common mantling zone: the Mt. Ślęża Massif, Kiełczyn Hills and Jańska Góra. It was created to protect extraordinary natural features (geology and geomorphology), as well as cultural heritage (palace-park village architectural assemblages, archeological sites). The Mt. Ślęża Massif is an island of crystalline basement rocks exposed from beneath the Cenozoic sedimentary cover in the central part of the Fore-Sudetic Block. The massif exposes one of the best preserved and complete ophiolitic sequences of the entire Variscan Belt of Europe. The sequence comprises, from bottom to top, serpentinites, gabbros, diabases, pillow lavas, and radiolarites, and it is intruded by a late-Variscan granite of the Strzegom-Sobótka Massif. Two major glaciations left large block-fields on the slopes of Mt. Ślęża. Apart from special geological aspects, Mt. Ślęża is a unique archeological site. The human settlings in this region date back to the Neolith, and the area is famous for several well preserved stone-rings and warship sculptures. That is why Mt. Ślęża is called the "Silesian Olympus" and is the nearest tourist and re-creation background for the city of Wrocław.



Fig. B 1-2. Mafic rocks of Mt. Ślęża plotted on multi-element variation diagrams. Squares - plutonic group, circles - subvolcanic/volcanic group. Left-hand column - incompatible trace-elements normalised to MORB; right-hand side column - REE normalised according to Sun (1980); a & b - metabasalts and metadiabases (higher plots) and metagabbros of the upper part of the plutonic assemblage (lower plots), c & d - mafic cumulates (based on Kryza & Abdel Wahed 2000).

#### Stop B 1/5 – Sobótka

Location: Sobótka town, morphological map of Mt. Śleża Massif Geology: the Ślęża ophiolite (Silurian/Devonian?): outline geology and petrology Leaders: Ryszard Kryza, Alfred Majerowicz & Piotr Gunia

The Ślęża ophiolite and other parts of the Central-Sudetic ophiolites and their lithology, geological position and ages are presented.

#### Stop B 1/6: Mt. Ślęża/Przemiłów

Location: 5.5 km ESE of Mt. Ślęża; abandoned quarry at Przemiłów Geology: the Ślęża ophiolite, lower part of the ophiolite suite: metamorphic peridotites (serpentinites)

Leaders: Piotr Gunia, Ryszard Kryza, Alfred Majerowicz

The serpentinites exposed at Przemiłów represent mantle peridotites, the lowermost member of the Ślęża ophiolite (Majerowicz & Pin 1994). Blocks and boudins of massive psedomorphic serpentinites are enclosed in sheared chrisotile-rich matrix. Locally, they preserve mantle-tectonite texture with bastite pseudomorphs after porphyroclasts of pyroxene surrounded by hour-glass pseudomorphs after olivine neoblasts. The primary mineralogy, deduced on CIPW norm, suggests they were mostly low-Al harzburgites and lherzolites (Majerowicz & Pin 1994) primarily equilibrated in the spinel-peridotite stability field. In the rock matrix, small relics of forsteritic-olivine occur, often surrounded by big flame-shaped antigorite; other constituents of the serpentinites are ameboidal chromian spinels, cloudy assemblages of magnetite microspherules and single tremolite-actinolite needles. Spinel/pyroxene domains, resembling the habit of garnet were found and suggested to indicate retrograded garnet peridotites (Dubińska *et al.* 2004). Occasionally, small apogabbroic rodingite bodies occur, surrounded by narrow chloritic blackwals. In their matrix, relics of ophitic integrowths of augite-diopside and framboidal grossularite are common. Veins of brownish vesuvianite occur sporadically. The rodingites can be classified as "shallow" type metasomatites.

According to Mierzejewski & Abdel Wahed (2000), the serpentinites display two deformational episodes: an earlier top to WNW thrusting along listric thrust faults, and a later top to ESE normal faulting due to relaxation of thrust blocks.

#### Stop B1/7: Mt. Ślęża/Tąpadła Pass

#### Location: 2.5 km SWS of Mt. Ślęża, ca. 150 m S of Tąpadła Pass Geology: the Ślęża ophiolite, contact zone between the serpentinites and gabbros Leaders: Piotr Gunia, Alfred Majerowicz, Ryszard Kryza

A contact zone between serpentinites and strongly sausuritized metagabbros can be observed in a crag and small abandoned quarry. The antigorite serpentinites were interpreted by Majerowicz (1981) as metamorphic peridotites, whereas the variable mafic/ultramafic rocks – as cumulates at a marginal part of the ophiolite body. Gunia and Sosnowski (2005, unpublished data) considered the antigorite serpentinites to occur as individual blocks several metres in size incorporated within strongly sheared "flaser" metagabbros. The character of contact plane varies from place to place, most often it is sharp and steeply dipping. Strong deformation of fine-grained "flaser" gabbros, and brecciation of accompanied serpentinites are also visible. In many places, the "primary" contact plane is obliterated by narrow fault zones containing mixed mafic and ultramafic components. Their origin is probably connected with deformation event D3 contemporaneous with the intrusion of the Strzegom-Sobótka granitoids. The structural features of the contact zone between tectonite and cumulate members of the Ślęża ophiolite are similar to those in the "Acoje" type ophiolite, with evidence of diapiric movements of mantle-derived inhomogenic material near the rift axis.

#### Stop B 1/8: Mt. Ślęża / Tąpadła Pass

#### Location: 2.1 km SWS of Mt. Ślęża, large crag and blocks on slope Geology: the Ślęża ophiolite, middle part of the ophiolite suite: layered gabbros Leaders: Alfred Majerowizc, Ryszard Kryza, Piotr Gunia

In crags and large blocks north of the pass, coarse-grained grabbros of the plutonic member of the ophiolite are exposed. They often display evidently igneous, ophitic texture and, locally distinct magmatic layering (alternating clinopyroxene-rich and plagioclase-rich bands, up to a few cm thick).

Generally, the gabbros exhibit N-MORB geochemical and isotopic characteristics, but some cumulates show various anomalies (Pin *et al.* 1988, Floyd *et al.* 2002).

In places, localized deformational structures can be observed. Abdel Wahed (1999) distinguished three deformational events in the basic member of the ophiolite: D1: west-directed tectonic transport, D2: top to NNE shearing (corresponding to NNE thrusting along the E & W Sudetes boundary ?), and D3: brittle deformation represented by variously oriented slickensides.

Kryza (in Majerowicz *et al.* 2000), based on the observed sequence of igneous and metamorphic minerals in metagabbros, distinguished the following stages:

- 1. magmatic stage: crystallization of gabbro followed by late-magmatic emplacement of diallagite pegmatitoids,
- 2. early low-temperature metamorphism, probably in rather static conditions (oceanfloor metamorphism?), evident from the presence of texturally early actinolite,
- 3. peak-temperature metamorphism recorded, e.g., by green acicular Mg-hornblende which defines the foliation in localized thin shear-zones in the gabbro,
- 4. fading (late) metamorphism, under decreasing temperature, and further replacing the earlier mineral parageneses, and associated with localized deformation in semibrittle- to brittle conditions.

Above the gabbros, Majerowicz (in Majerowicz & Pin 1994) described the so called "roof assemblage" of the plutonic/subvolcanic zone of the ophiolite. The rocks in this zone display highly variable textures: fine-grained metagabbros and diabases with ophitic, subophitic, porphyritic and glomeroporphyritic textures are embedded in fine-grained or aphanitic groundmass. Locally, near the base of the volcanic group, sheeted-dyke-type structures have been described (op. cit.).

The volcanic group shows geochemical similarities but also distinct dissimilarities compared with the plutonic group, which implicates complex petrogenetic processes involved in magma generation and differentiation, and possible (tectonic ?) discontinuities between plutonic and volcanic parts of the ophiolite.

Dark radiolaria-bearing metacherts may represent sedimentary cover of the Ślęża ophiolite, but their contact with the magmatic members is masked by the Cenozoic deposits.

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B2.

#### N contact aureole of the Karkonosze granite

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**Abstract:** field trip course runs within szklarska poręba hornfels belt. during the field trip the mineralization accompanying metamorphic, metasomatic and hydrothermal processes, associated with the karkonosze granite intrusion, will be shown.

**Key-words:** skarn, hornfels, wollastonite, vesuvianite, grossular, diopside, andalusite, cordierite, Izerskie Garby, Zakręt Śmierci, Zbójeckie Skały, Pyrite Mine

#### **Geological setting**

Szklarska Poręba hornfels belt is a fragment of the Karkonosze-Izera Block and is located at the contact of the Karkonosze granit with mica-schists of the Izera metamorphic complex (Borkowska 1966; Smulikowski 1972, Mazur 2002, Oberc-Dziedzic 2007) (Fig. 1). The age of the Karkonosze granite is estimated at  $329\pm17$  Ma (Duthou *et al.* 1991). The Izera Block consists of gneisses, granite-gneisses and granites of the pre-Variscide age. The granite protolith was dated by different methods on 515-480 Ma (Borkowska *et al.* 1980; Korytowski *et al.* 1993; Oliver *et al.* 1993; Żelaźniewicz 1997; Kröner *et al.* 2001). Within gneisses and granites several belts of mica-schists have occurred. Szklarska Poręba schist belt, which was at the immediate contact to the Karkonosze granite, was transformed into cordierite-andalusite, biotite hornfelses and Ca-skarns. The age of contact metamorphism is dated on  $333\pm4$  Ma (Fila-Wójcicka 2004). Pegmatites and late hydrothermal veins are cutting the metamorphic rocks.

#### Stop 1 – Stanisław Mine (20 min by bus from Szklarska Poręba)

The Stanisław Mine is the highest active mine in the Central Europe (1088 m a. s. l.). Mineralization of the mine is confined to Izerskie Garby dislocation zone, located between hornfelses (in SE) and gneisses (in NW) of the Karkonosze-Izera Block (Lewowicki 1965) (Figs. 1&2). The dislocation runs in the distance of a few kilometers from Jastrzębia Góra in NE through Piaskowa Góra, Rozdroże Izerskie, Izerskie Garby into the Karkonosze granite on S-side of Wysoka Kopa. The dislocation is dipping steeply (65°) to SE and its width ranges between 100 and 300 m (Szałamacha 1965; Szałamacha & Szałamacha 1966). Quartz is a predominant mineral filling.



Fig. 1. Geological map of the Szklarska Poręba belt (after Kozłowski 2002, modified). 1- quartz vein, 2- hornfelses, 3- Karkonosze granite, 4- Izera gneisses and granites, 5- mica schists, 6- faults, 7- quarry, 8- stops, 9- state boundary

The Stanisław mine excavated pure quartz from XIII century. From this locality the samples of rose quartz colored by hematite are known. The largest rose-quartz crystal reached 50 cm in length. Apart from quartz veins a silification of both gneisses and hornfelses is noted. Ca-skarns and hornfelses are the most interesting mineralogical object in the Stanisław mine. Wollastonite, grossular-andradite, vesuvianite, diopside-hedenbergite, epidote, calcite, fluorite are the main minerals of skarns. Monazite, zircon, titanite, allanite, calcite, pyrrhotite, pyrite, chalcopyrite are accessory minerals (Fila-Wójcicka 2000; Pieczka & Kraczka 1998; Karwowski *et al.* 1996).

Aggregates of white massive wollastonite up to 2 m in size are noted. Vesuvianite crystals form aggregates up to 20 cm. Xenomorphic garnet blasts are up to 3 cm in diameter while idiomorphic garnet crystals reach 1 cm in size.

Numerous vein-like pegmatite bodies occur at Stanisław mine. Minerals such as: tourmaline, rutile, apatite, chlorite, löllingite, native bismuth, cassiterite, scheelite, feldspar, muscovite, biotite, fluorite, zircon, monazite, xenotime, were described by Długoszewska (2005).

A late hydrotermal mineralisation is also present as fluorite-apophylilite-quartz-calcitestilbite-chlorite association (Kozłowski 1978). Recently among the hydrothermal mineralization vanadinite (Szełęg, 2008) and mottramite (Szełęg, unpublished) were discovered.

Andalusite crystals up to 3 cm in length, schörl and pinite pseudomorphs after cordierite occur within hornfelses.



Fig. 2. Geological sketch of the Stanisław mine in the Izerskie Garby Mt. (after Janeczek *et al.* 1991, modified).

#### Stop 2 – Zakręt Śmierci ("Death Bend") (25 min from Stop 1 by bus)

A road bend from Szklarska Poręba to Świeradów is named Zakręt Śmierci (Death Bend). The road bends at near 185° in this place.

<sup>1-</sup> gneisses, 2- hornfelses, 3- quartz vein, 4- silification zone, 5- outcrop of skarns

Rocks observed above the Death Bend constitute of cordierite-andalusite and biotite hornfelses of Szklarska Poręba belt. Thin inserts of amphibolites, pegmatite and quartz veins are associated with hornfelses. That place is a picturesque scenery, where panorama to the western part of the Karkonosze ridge can be seen (Fig. 3).



Fig. 3. A view to the western part of the Karkonosze Mts. from Death Bend.

#### **Stop 3 – Zbójeckie Rocks** (15 min by foot from Stop 2)

Cordierite-andalusite hornfelses are called Zbójeckie Rocks. That place presents a contact of the Karkonosze granite with hornfelses (Fig. 4). The granite body shows a zonation parallel to the contact surface (Żaba 1979). A pegmatite zone is the most interesting in respect to accessory minerals as: apatite, arsenopyrite, bismuth, chalcopyrite, fergusonite, magnetite, pyrite, tetrahedrite, thorianite, wolframite (Gajda 1960 a, b). Hornfels samples with andalusite crystals up to 4-5 cm in length are known from this locality.

#### **Stop 4 – Pyrite adit** (7 min by foot from Spot 3)

The first documented notes about pyrite exploration in this place were dated for 1530. Pyrite was used for sulphuric acid production in manufactory located nearby. 400 ton of pyrite per year were mined from 1772 to 1787. Besides pyrite lead and silver ores were also explored. Exploitation of pyrite was finished at the turn of the XVIII/XIX centuries. Currently adit and dump could be observed.



Fig. 4. Contact of cordierite-andalusite hornfelses with Karkonosze granit on the Zbójeckie Rocks.

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Post-Conference fiels trip - Sunday, September 14, 2008

B3.

#### Geotouristic tour in Szklarska Poręba

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**Abstract:** A short and easy walk with visits to a local Mineralogical Museum, Karkonosze Centre for Ecological Education and, weather allowing, to the picturesque Kamieńczyk waterfall.

Key-words: geotourism, Mineralogical Museum, Centre for Ecological Education

#### Introduction

Szklarska Poręba is situated in the south-western part of Poland in Jelenia Góra district and Lower Silesia Province, about 130 km from the Lower Silesian capital of Wroclaw, almost at the meeting point of the borders of three countries: Poland, Czech Republic and Germany, in Karkonosze and Izery mountain range.

The name Szklarska Poreba means 'glass forest clearing', and actually comes from the local glass making industry. For centuries the manufacturing of glass and glass products has been the chief driving force behind the development of the town. Szklarska Poreba is the site of the first glassworks to be founded in the Sudeten Mountains, which occurred as early as the 14th century.

Szklarska Poręba is regarded one of the best tourist centers in Poland. The city is picturesquely located at the bottom of Szrenica Mountain (1362m a.s.l.) at the altitude of 440 – 886m a.s.l. Enormous tourist advantages and favorable location makes Szklarska Poręba an attractive centre in both tourist and economic respect (fig. 1). The climate is high mountain, with relatively low temperatures, a lot of sunshine, low humidity and snow cover remaining for about 110 days each year. Climatic and relaxation advantages of Szklarska Poręba allow for an active way of spending time not only in winter season, but practically all year round, by offering hiking along tourist trails, the network of mount bike paths and the rich offer of cultural activities e.g. museums.

Around Szklarska Poręba there are about 100 km marked trails. From their hub in the heart of the town, the particular paths: the red, blue, green, black and yellow one, run in a shape of a star towards the Karkonosze and Góry Izerskie mountains. There is a two-stage chairlift to carry people up Mt Szrenica, to an elevation of 603 m. The main part of Karkonosze belongs to the Karkonoski National Park, which was declared by UNESCO one of the World Biosphere Reserves (Karkonosze/Krkonosze). Along the paths there are the characteristic rocks and rock groups, typical for the Karkonosze Mountains as well as beautiful waterfalls and excellent lookout points.



Fig. 1. A view from Szklarska Poręba city centre (photo by: B. Kajdas).

#### Stop 1. The Mineralogical Museum

Mineralogical Museum in Szklarska Poręba has one of the most particular geological collections in Poland. There are gathered valuable mineralogical and paleonthological specimens. Almost 2500 rocks and minerals from all over the world can be admired in the museum and one exhibit from space- Gibeon meteorite. The separate department of museum is devoted for fossils including reconstructions of dinosaurs' skeletons and an egg of a dinosaur. In front of the building there are trunks of carboniferous wood. The collection comprised also the biggest in Poland, 10-karate diamond in its natural rock-stolen in 2002. Now the glass box contains its description and photos. Mineralogical Museum is located on 20 Kilińskiego str.

#### Stop 2. Karkonoskie Center for Ecological Education

Karkonoskie Center for Ecological Education in Szklarska Poręba is an outpost of Karkonoski National Park which coordinates ecological education tasks. In Karkonoskie Center for Ecological Education a lot of information about the regions' nature – the world of animated nature and the inanimate side of the Polish and Czech mountains are presented in a very attractive way. Tourist paths and protected areas are presented in the Centre. A few rooms provide visitors with a virtual tour of the post-glacial cirques, moors, fauna, flora, and information about how humans have impacted on mountain life. Visitors can admire huge panoramas from Śnieżka, Chojnik, "Samotnia" shelter, Szrenica, Owcze Skały, Studnična hora, Medvědin and from few other places in Polish and Czech Karkonosze, and mockup of Karkonosze Mountains. Karkonoskie Center for Ecological Education organizes also field trips and classes in chemical and microscopy laboratories for
students, pupils and groups of visitors.

#### Stop 3. Szklarka Waterfall or Kamieńczyk Waterfall

Several scenic sights are within walking distance the Szklarska Poręba centre. Only 1.5 km away from the town, near the road to Jelenia Gora, one can admire the popular and beautiful Szklarka Waterfall (fig. 2), the loveliest in the Karkonosze Mountains. It is situated 520 m a.s.l. and is 13.3 m high. Water is falling down forming characteristic wide cascade narrowing at the bottom. Its beauty was already well known by the 18th century. Another possibility, depending on the weather is a visit at the Kamieńczyk Waterfall (fig. 3). It is situated 1.5 hour walking along tourist path. Kamieńczyk Waterfall it is the biggest in Polish part of Karkonosze. Kamieńczyk Stream has its spring at Szrenica Meadow 1260 m a.s.l. The waterfall is 27 m high and falls down in three picturesque cascades. It may be admired from two spots. The upper part of the waterfall may be vied from the viewing area however the waterfall is much more beautiful when vied from the Kamieńczyk Canyon.



Fig. 2. Szklarka Waterfall (photo by: B. Kajdas).



Fig. 3. Kamieńczyk Waterfall (photo by: B. Kajdas).

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